

Investigation And Developing Of Double Layer Capacitors For Start Of Internal Combustion Engines And Of Accelerating Systems Of Hybrid Electrical Drive

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ABSTRACT

In present report a short description of the complex of applied investigations and project development which has led us to making a family of DLC systems to start Internal Combustion Engines (ICE) is given. Much attention is paid to investigation of obtaining parameters of starting Supercapacitors (SC) and optimal design.

This report reveals:

- The main results of testing of the SCs being produced in small scale in Russia;
- The advantages of the system Battery + SC to start ICE over usual starting batteries;
- The aspects of use of the DLC system for hybrid vehicle;
- The project data of accelerating- recuperative block based on DLC with aqueous electrolyte.

As a result there's given a conclusion that DLC based on aqueous electrolytes with specific parameters lower than of DLC with non-aqueous one can be successfully used to start ICE and for electrical vehicle thanked to their high power and efficiency at high discharge current.

1. Introduction

It is widely known, that capacitor and DLC in particular, present higher power in comparison with chemical power sources. Besides, the wide temperature window at exploitation, long service life at cycling, perfect maintenance free - all these are indisputable advantages of DLC (Supercapacitors, Ultracapacitors) over usual storage battery.

At the same time, their specific energy store is by an order lower than of storage batteries.

Autonomous power source, if being applied to start internal combustion engine (ICE) must possess high power (for starter rotation). Long estimations of start process in real conditions and of energy balance in vehicle allow us to make a combined system for ICE, where the functions of starter cranking (power output) and service the other affected loads are considerably separated. Right here is the place for powerful Supercapacitor (SC) which is able to rotate starter and be charged by storage battery during interval. Storage battery itself may be not -t starting one as it is, and can present, consequently, longer service life and be maintenance free or seated as well.

The conception of separating the functions of energy store and of power output, which was realised through the combined system SC + Storage Battery, allows to join together the positive qualities of these two types of power sources, and as well to obtain high service life, maintenance free of on-board power source able to guarantee start of ICE at any weather conditions and any state of charge (SOC) of Storage battery.

The present report target is to show in brief the research, development and project-works carried by ELIT Go. during last 5 years. Those works lead us to making a wide range of DLC for start of any types of ICE being produced in Russia.

2. Power of start and prerequisites of use of SC

A great number of standards having been created by starter batteries manufacturers, do not contain information of ICE-start real process, and they are just known as average approximation satisfying battery and vehicle manufacturers. The real information of the process, where current, voltage and active strokes of engine are fixed, one can find in series of oscillogrammes only, read at

different temperature regimes and state of engine.

Starter as electrical machine of DC has its own full internal resistance at transient start moment. Process of start is not stationary and it is characterised by increased need in energy at initial moment to shift a loaded shaft from the dead point, and by decreasing of energy consumption at picking up speed. If we take a look at a real process of start with use of starting battery, we can see the starting battery not utterly meet the start target, because it does not provide maximum power at the initial stretch of time.

Amplified calculations, done according to oscillogrammes of real starts in accordance with changing level of starter energy consumption, show insignificant energy consumption at start of engine, if to compare it with full energy store of board starting battery. So, at start of engine 1500 cc the consumption is 1,000-2,000) J (depending on engine state), which is just 0.008% of the energy stored in starting battery (55 Ah, 12V,- 2,376,000 J).

Thus, the above data of power are the initial requirements towards energy store of SC. In this case the internal resistance of SC should stay rather low to provide enough efficiency of energy transmission consequently to well known correlation (I):

R_0/R_l	: 0.01	:0.1	:0.5	:1.0
Efficiency %	:99	:91	:67	:50

where: R_0 -full internal resistance (ESR)of SC;

R_l - resistance of discharge load.

Board energy consumption (with exception of start) significantly depends on type of vehicle and on available of conveniences for driver (condition and others). The works on complex analysis of energy consumption were carried out on all main types of Russian vehicles by employees of Moscow Automobile-Mechanical Institute. The works showed that the whole energy consumption (with exception of start), capacity of storage battery may be lessened to 1.5-2 times if the battery serves to board consumer only.

Basing on the above, we can declare that Starting SC can be inserted under vehicle cowl at the expense of decreasing of capacity and dimension of board battery. That decreases neither start characteristics nor comfort.

3. Research of the Main Requirements towards Starting SC.

Determining of parameters of SC taking into account diminished dimensions of volume of starting battery and the peculiarity of the battery allocated in car and lorry, and the balance of energy consumption at start shows the next performances:

weight (without increasing of total weight of the system SC + battery)

-for cars - 4...8 kg;

-for lorries - 12..36 kg.

volume of SC (without increasing the total volume of the system SC+battery)

-for cars - 1...5 Lit;

-for lorries - 5..12 Lit.

Internal Resistance

The initial value of start current at low temperature is equal to the current of short circuit and, even for middle class vehicles it can be 400...500 A at voltage drop up to 8 V when nominal is 12 - 14 V. That is caused by momentary value of internal resistance 0.016 - 0.02 Ohm. If efficiency of energy transfer is 80 - 90%, the ratio of these values gives us ESR of SC 0.002-0.006 Ohm.

In the same manner we can find out ESR of SC for lorry, and it is 0.003-0.005 Ohm.

Operating voltage

Average operating voltage for cars is 12V;

Voltage of floating charge at exploitation -13.5-14.5 V;

Overload by voltage of alternator at low temperature -15-16.5 V (several tens of minutes)

For lorries the average value is 24-26 V;

Voltage of floating charge - 28-29.5 V;

Overload by voltage - 30-32 V.

The end of discharge voltage of SC is calculated by voltage of turning-off starter relay, and it is 5-6 V for cars and 12-15 V for lorries.

This parameter is very important, because it sets the limit capacity (energy) of SC in the frame $U_{oper} \leftrightarrow 0.5 U_{oper}$.

Full Energy Store

Taking into consideration the fact that in a vehicle, in any case, there's a storage battery, we proceed from the conception:

Full energy store of SC must provide at least 1 guaranteed start of engine independently on environment and state of the engine.

If start failure is caused by fault of vehicle circuit, the SC won't be discharged perfectly. If the start failure is caused by fault of fuel system, the SC can be perfectly discharged. But in both these cases, after it has been connected to battery, a rather fast (6-30 sec) restore of energy is possible. It depends on state of discharge of the battery.

As it's shown by additional research, even a battery with SOC=0% is able to charge SC within acceptable time (several minutes) with small current enough to make an effective start.

SC is not an "ideal" capacitor and while designing we deal with real thickness of electrodes and with concrete value of ions mobility in electrolyte. That means we deal, in essence, with existing charge distributed in volume (capacity). Naturally the energy store depends on rate of it's output, that is discharge current, and the higher is its density, the lower is effectiveness of energy store is. Herein is some analogy of Peikert formula for traditional power sources. In the main, for SC the constant of time can be used to determine the capacity in dependence on time of its discharge.

Efficiency of energy output depends also on such factor as temperature which decreases ions mobility at decreasing of temperature. The influence of the above to the factor describes ESR of SC and its dependence on temperature rather well, but it's unacceptable at all if the real electrodes are thicker than 0.5 mm.

Practical research show that the energy store must be 2-3 times higher than effective one (for starting needs only).

As it was said in item 2 of present report, to start engine 1500 cc, just 1000-2000 J is needed, but in practice, with taking into consideration all the above, it's expediently to have energy store 3.5-6 kJ.

It's necessary to note, that the definition "full energy store" is very conventional. We defined it as "energy having been put to fixed load". The value of the load should be such, that in case of its further increasing (decreasing of discharge current density) the efficiency of output energy increases inconsiderably. For starting SC the value is 1 Ohm and it is approved by a big number of customers.

Taking into consideration the voltage of turning-off relay of starter, the above "full energy store" should be calculated by volume put into voltage window $U_{oper} \rightarrow 0.5 U_{oper}$.

Limit Level of Specific Energy

Practical research and analysis of types of Russian vehicles allowed us to determine the cut-off levels of specific energy. The lowest level will be a serious problem of arrangement and distribution of the weight of starting system

for cars the value is	0.8 kJ/kg; 1.0 kJ/lit
for lorries it is	0.6 kJ/kg 0.8 kJ/lit.

The above figures for lorries can be explained by higher, in comparison with cars, admissible diminishing of board battery capacity and by engine spaced apart.

Of course, auto manufacturers strive for increasing of this parameter with simultaneous cost reduction.

Leakage current

There exist 2 main ways to use SC in the starting systems SC + battery. To start lorry and more heavy vehicles, where starts are less frequent than of cars, the principle "prepare-start-forget" is very suitable. In this case SC charges from battery right before start, during pre-starting preparing (10 sec-2 min). The rest of time the SC is discharged or partially discharged. Here the leakage current is not important, because it does not influence on balance of board energy, and even if leakage current discharges SC to "0", then during pre-starting preparation the SC will be charged.

But it's going on more difficult with the system where SC is electrically connected to battery or connected through current limiting shunt. Critical value of leakage current is estimated mainly for every type of vehicles, with taking into consideration the admissible loss of the main battery capacity at keeping the vehicle with SC connected to battery. Another fact, that start is also possible at SOC of battery less than 30% at temperature to -20°C , must be taken into account too.

In the whole, the formula to calculate critical value of leakage current is

$$I_1 = \frac{C(1 - K)}{24T}$$

where:

I_1 - critical value of leakage current (A);

C - capacity of board battery (Ah);

K - coefficient signifying admissible residual capacity of battery (30% = 0.3);

T - time of inaction of vehicle with SC connected to starting battery (days).

For example: I1 for vehicle with storage battery 30 Ah, residual SOC 30%, inaction for 6 days, is approximately 146 mA.

But in practical designing and exploitation of SC on a board of vehicle, the leakage current value is (as a rule) 40-60 mA after several minutes, and 2-10 mA after several hours (output to a little charging part of selfdischarge curve).

Service Life

Service life is a measure of SC advantages over traditional starting battery. Auto manufacturers and auto users would like to get starting SC with service life equal to service life of vehicle - 10-12 years. Thus, SC must become an irreplaceable part of vehicle like a vehicle body or alternator. Data of analysis of statistic of different types of vehicle exploitation allow to determine the frame of their cycle life, as the next:

- for car	70 -100 thousand cycles
- for lorry	35 - 50 thousand cycles
- for locomotive engine; power generator	10 -20 thousand cycles

As a rule, these parameters are not serious problem for SCs and they are already confirmed by SC- designers in the world.

Temperature Range

Temperature range, adduced in the article by J. DeGaynor (2), is -40...+125°C. The range is quite suitable for vehicle manufacturers, because it allows them to take no special measures to arranging and protection of SC in or out of engine compartment.

However, from the point of view of any designer of chemical power source, the keeping of start parameters at necessary level of exploitation (startability) and at the above service life and temperature range is impossible.

In the main, it's possible to use SC system with solid electrolyte at +125°C and to obtain required service life. But dischargability with high current at normal temperature and especially at low temperature tends to zero. For liquid electrolytes, stable operation for many years at temperature >70°C is a problem.

In the given situation, we propose the next solution of the problem, which is able to satisfy the both party. We should not try to excessive unification of SC, but to develop different families of SCs by the way of regions of their exploitation. Everyone knows of existing of different types of starting batteries, such as tropical, for normal temperature, for cold, etc.

In ELIT design the next types of SCs by temperature are used:

1	-40°C ... +60°C
2	-20 (-25) °C ... +70°C
3	-10 (-15) °C +80°C (max. temperature for several hours); +100°C (max. temperature for tens of minutes)

Note: The hereabove temperature influencing immediately on block of electrodes without special protection is meant.

Maintenance

The necessity to maintain power sources during exploitation is caused, as a rule, by loss of electrolyte - it's **entrainment** as aerosol and/or gases as electrolyse product of electrolyte . At inserting of SC into vehicle, the emission of aerosols, active corrosion and toxic substances of

electrolyte to environment is inadmissible. In spite of forced ventilation under engine hood, vehicle manufacturers are all against inserting of power sources emitting even a small quantity of gas. And in any case, the necessity to maintain power source, even periodically, leads to rising of exploitation expenditures and decrease commercial value of the product.

ELIT specialists' design proceeds from the pre-requisite that SC for vehicle application must be perfectly maintenance-free during all its service life and must not emit any substances into environment. Presently in the world enough experience of designing of power sources is accumulated perfectly maintenance free for 10-15 years (the power sources are designed specially for military purpose) and the problem can be supposed to be solved.

Specific effects

Enumeration of specific effects is given in the article by J. DeGaynor (2) rather enough. The value of vibro-proofness is not a problem for the technology of modern construction materials. The same relates, as well, to proofness against phenomena connected with vehicle exploitation, such as mud, moisture, fuel oils, etc.

Cost Factor

Vehicle manufacturers suppose that the cost of the System SC+battery must be at least not higher than the cost of the battery used at the vehicle before. In some degree they are right, because any rise of price of vehicle complete set rises the price of the vehicle in whole and reduces its "saleability", especially at severe competition. But presently the price of the System is higher than of battery to 1-3 times. It's caused, firstly, by small scale production of SC and by high specific volume of labour cost. In Russia all the raw materials should have been cheaper and available, but for today's Russian unhealthy economic with unexpected jumping of prices. Of course, we can expect cost reduction in case of stable mass production.

However, even now at very unfavourable coincidence the use of SC for start is very advantageous for vehicle users because during the whole service life of a vehicle equipped with the new starting system, the user needs not to change it several times.

In some issues of "The Battery Man" and the "Batteries International" of some last years there's given an analysis of starting batteries failure. The average data of battery service life is between 2.5-3.5 years, in spite of manufacturers guaranty 4-6 years. One can give me an example as objection, that he knows the cases when the service life was 5-6 years. It's rather an exception than a rule, because some of batteries are failure in a year of work. It is a city operating cycle of taxi in hot climate regions.

Thus during 10-12 years of vehicle exploitation we have to change 3-4 batteries with total price exceeding the price of the System SC+battery.

We must not forget as well the fact, that consumer buying the starting system has got additional advantages, such as guaranteed start at any condition, diminution (or elimination) of battery maintenance. But it's a task for advertising and market stage of SC production.

There exist some types of materiel with engines whose start must be independent either on their state or weather condition. These are special vehicles - Ambulance, Police, Rescue and other. Use of a high cost SC in these vehicles is always authorised.

Summarising the above, we can suppose the one-and-half or two times exceeding of price for the new starting system, as compared with starting battery, is enough acceptable on the stage of wider market of automotive application.

Technical specification of SC for start of ICE

Tab. 1.

PARAMETERS		VALUES	
		PASSENGER CARS	LORRIES
1. Operating voltage	(V)	12	24
1.1. Average		13.5-14.5	28-29.5
1.2. Floating		15-16.5	30-32
1.3. Maximal		5-6	12-15
1.4. Minimum			
2. Energy store	(kJ)	4-10(12)	15-40 (50)
3. Internal resistance (ESR)	(Ohm)	0.002-0.006	0.003-0.005
4. Leakage current	(mA)	<50	<100
5. Weight	(kg)	4-8	12-36 (40)
6. Volume	(lit)	1-5(8)	5-12 (16)
7. Energy density			
7.1. Limit level			
	kJ/kg	0.7	0.6
	kJ/lit	1.0	0.8
7.2. Practically used			
	kJ/kg	0.7-1	1-1.2
	kJ/lit	1.2-1.7	1.5-2.5
8. Service life		9-12	10-14
8.1. Years		70,000-100,000	35,000-50,000
8.2. Cycles			
9. Temperature range	(°C)	from -40 to +80 (100)	
10. Maintenance		no maintenance within service life	
11. Specific effects		the same as 2 for SLI batteries	
12. Cost factor (SLI battery = 1)		1-1.5	

4. Development of Starting SC

In the previous parts of present report the author has shown probably too detailed some of SC parameters, and it is done in order to lead the audience closer to choose the system or the conception of starting capacitor.

4.1. Choosing Of Types Of Electrolyte

In usual design of SC containing collectors, polarizable electrodes, separator and the electrodes and the separator impregnated with electrolyte, electrolyte is the critical link of high power. Electrolyte solution must contain sufficiently high concentration of solvated ionogen to form a dense part of double layer and maximal ion conductivity. The last one dominates for starting SC.

For maximum practical use of applied research, we have carried out measurement of specific resistance of standard cells (Fig. 1) with different types of electrolyte therein.

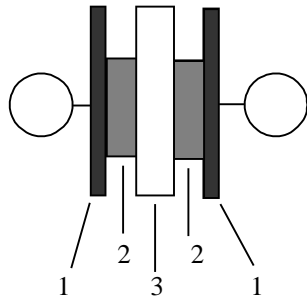


Fig. 1

1. Low resistant collector, inert to the electrolyte to be examined.
2. Polarizable electrodes made of activated carbon, impregnated with electrolyte to saturation of sorbing volume.
3. Separator with increased capillary properties, impregnated with electrolyte to saturation.

Note: 1. For solid electrolytes a special design was used.

2. Total thickness of the cell is <0.8 mm.

Results of investigation at normal conditions are given in Table 2

Table 2.

Type of electrolyte	Specific resistance of cell (Ohm/cm ²)
1. Solid electrolyte	>15(10.2-RbAg ₄ J ₅)
2. Non-aqueous electrolyte with combined solvent	>12
3. Aqueous electrolyte (acid, alkaline)	0.06 - 0.4

The data rather well correlate with the data from booklets (3,4) of SC manufacturers.

Efficiency At Decreased Temperature

Investigation showed that we can say nothing positive of efficiency of non-aqueous and solid electrolyte at -20°C, because their conductivity decreases to tens times (perfect freezing to equal temperature of electrolyte and of freezing chamber).

In the case of solid electrolytes use the ions mobility in vacant place of conductivity of crystal sharply decreases. And non-aqueous electrolytes are characterised by ionogen salt precipitation caused by loss of solvent properties of organic electrolytes.

In the main, the traditional sphere of application of DLC with solid and non-aqueous electrolytes is Memory Back Up (UPS). The sphere offers, as a rule, discharge with small current which often can be compared with DLC leakage current. So, the developers and manufacturers of DLC for UPS are not far from truth when speaking of not sufficient decreasing of output capacity at decreasing of temperature.

In the case of starting SCs, the high discharge current at increasing of ESR leads to considerable voltage drop and output a small part of accumulated energy at voltage lower than 0,5 Uoper. Efficiency of these systems in the regime of start at temperature -40°C is impossible in practice without special pre-heating.

The aqueous solutions of electrolytes decrease their conductivity to 1,5-2,5 times at -20°C and to 3-5 times at -40°C and they are more preferable to be used in starting SCs.

Efficiency At Increased Temperature

Increasing of temperature influences positively on reduction of ESR and on efficiency of output energy. But in the same time the leakage current of DLC is increased. It can be easily explained by growing of ions mobility and by break of dense part of DLC by the ions oscillation caused by temperature.

In the main, liquid electrolytes can operate normally at temperature up to +80°C. But non-aqueous electrolytes have property of increased volatility of solvent and of their ability to permeate through polymer sealant. That leads to constant loss of solvent, to increasing of ionogen concentration and finally to growing of ESR. The other problem of aprotic systems is flammability and explosive of ionogen solvents. In practice the operation of non-aqueous electrolytes is limited by temperature ~+60°C to save acceptable duration of service life.

The problem of loss of water is a property of aqueous electrolytes as well, nevertheless the problem of design of sealant against water steam is rather easy to solve, if compare with aprotic systems. By the way they are more safe at critical seal failure.

Solid electrolytes are the leaders in stability at increased temperature. They are able to grow their conductivity considerably. The temperature of +100°C is not an obstacle for them. Nevertheless, even in such conditions their conductivity is lower than of aqueous solutions, and the system RbAg_4I_5 and alike with their best performances are not commercially acceptable to make a SC with high energy capacity because of too high price of components.

In this item I specially do not mean the advantages of aprotic electrolytes because of their high U_{oper} of a single DLC, which allows to obtain considerable increasing of specific energy. In this item the rate of energy output and power are regarded as of paramount importance.

Taking into account that DLC with aqueous electrolytes excel in the limit level of specific energy not mentioned in item 3, we suppose their use for starting SC is more expedient by sum of the above positive phenomena of exploitation.

From the point of view of design, alkaline electrolyte is more preferable than other aqueous solution, because it allows to use wide-accessible and cheap steels and polymers.

The concentration of solution is selected near the point of maximal conductivity and can be changed in dependence on duration of service life and typical conditions of exploitation. It's possible to use some special additives increasing soaking properties of electrolyte and some stabilisers, as well.

4.2. Polarizable Electrodes And Separators

In today's world a great number of activated carbon materials is being produced, the materials are suitable to be used in polarizable DLC electrodes. ELIT Co. carried out testing of some powdered carbons and woven sorbents being produced in CIS and Russia. The principle mutual dependence between critical specific energy, specific capacity of carbon, specific surface area of carbon for KOH solution with concentration 20-35% was found. It was found, too, that lower level of specific surface area corresponding to critical level of specific energy is on the borderline 850 m^2/g , that corresponds to specific capacity of dry carbon 85-100 F/g.

The practical experience of production shows, that more beneficial is $S_{\text{spec}} = 1200\text{-}2000 \text{ m}^2/\text{g}$ (140-200 F/g). Increasing of specific surface area, which directly increases capacity of polarizable electrode is higher than that value and causes sharp rising of price. Besides, the carbon with extreme activated surface has a big portion of functional groups, existing of which not always leads to better sorption of electrolyte neither to forming of double electric layer. We have noted that "overactivated" carbons present higher resistance by volume and contact (carbon- collector).

Also we must note, that the dependence is right for aqueous solution KOH only, which is either confirmed by estimation of Alupower (5).

For other types of ions it's necessary to carry out testing because of existing of the effect of specific sorbtion when using carbons with different functional surface groups.

As a rule, polarizable powder conductive electrode contains always from 3 to 15% of conductor (carbon black, graphite, metal powders) to reduce volume and contact resistance.

To the mixture of carbon powders up to 10% of binder can be added in dependence upon method of polarizable electrode formation. In the case of use of woven carbon materials it's usually unnecessary to use additional volume.

Traditional design of DLC with 2 polarizable electrodes contains 2 capacitors in an element. Investigation of electrochemical capacitance of every single capacitor (that means specific full capacity) in the whole volume of electrolyte showed that capacity of cathode ("-") is higher than of anode ("+") 1,2-1,5 times. In the main it let optimise quantity of active material in every polarizable electrode. But in this case DLC becomes "polar" (6).

Problem of choice of separator is closely connected with dozing of electrolyte into extremely limited volume of thin cell. The separator, naturally, must hinder to appear electronic conductivity and increasing of leakage current. To obtain this the minimal diameter of the pores of separator must be lower than of carbon particles or diameter of monothread in woven polarizable electrode.

It's desirable, also, to have enough sufficient factor of separator pores sinuousness to escape electrophoretic move of particles of polarizable electrode, la principle, to get the aim the separator able to swell with electrolyte such as cellulose hydrate films, films made of grafted by radiation polyethylene and other may be used. Nevertheless their volume of electrolyte is not considerable. And to make the service life of DLC longer than 8 years it's expediently to have some abundance of electrolyte. It's necessary to compensate the loss of electrolyte at long period of exploitation. Analysis of DLC parameters change during cycle life testing showed in the 1st half of service life increasing of capacity and decreasing of ESR of DLC. It's connected with permanent moisten of new areas of polarizable electrode surface with electrolyte. Some of these areas couldn't be moistened at the steps of production of DLC. It's naturally that the part of electrolyte moves out from separator because capillary properties of active carbon in micropores is considerable higher than of separator. There exists also unavoidable loss of electrolyte for its migration onto surface of collector, penetration into the polymers of sealant, and partial decomposition at extraordinary situations (exceeding of operating voltage). At not sufficient electrolyte dozing , after some period of operating time ESR increases for re-distribution of electrolyte from separator.

On the other hand, over-abundance of electrolyte makes serious problems with sealing of cell and with saving the necessary level of resistance of SC isolation.

Optimisation of dozing led to necessity to use fibrous separators, which has maximal capacitance by electrolyte. The best for this are special types of paper and non-woven polymers with active functional surface groups.

4.3. Collector Systems, Sealing

As it was mentioned above, use of alkaline electrolyte allows to use wide-accessible types of steels for collector systems.

For system of power output the design solution must mind the shortest way for current. In such design the traditional scheme of battery with upper and side terminals is not suitable., because it admits local areas of concentration, critical section and not effective use of volume. It's neither expediently to use wound design, because thin electrode increases quantity of spires in a roll and leads to increasing of inductive part of internal resistance.

Bipolar design is the most ideal for such power sources with current transmission in normal to collectors. And at the same time, when thin foils are being used, the influence of specific volume resistance of collector material is of no importance, and at the 1st stage there appears the influence of contact resistance collector-carbon electrode.

ELIT Co. studied properties of surfaces in the area of current transmission well enough, and the necessary parameters of contacting materials are estimated (7).

We found that inconsiderable changes in quantity of surface can change internal resistance of DLC up to an order. These performances are the main at input control over collector material at production of DLC.

Use of metal conductors contacting with electrolyte solution makes problem with reliability of sealant. In this case the known effect Marangoni begins functioning • moving of electrolyte film along charged surface.

In practice, all the known compounds and seals being alkaline resistant and possessing enough adhesion to metals, turned over not to be useable, because the front of electrolyte film brakes adhesive interaction in the interface metal-polymer. And electrolyte wastage was diagnosed only several months later. We specially produced a special compound, emitting a special neutraliser for electrolyte from the volume of polymer into a borderline, and automatically strengthening the seal properties when coming in contact with alkaline (8).

4.4. Description of Standard Design of Starting SC

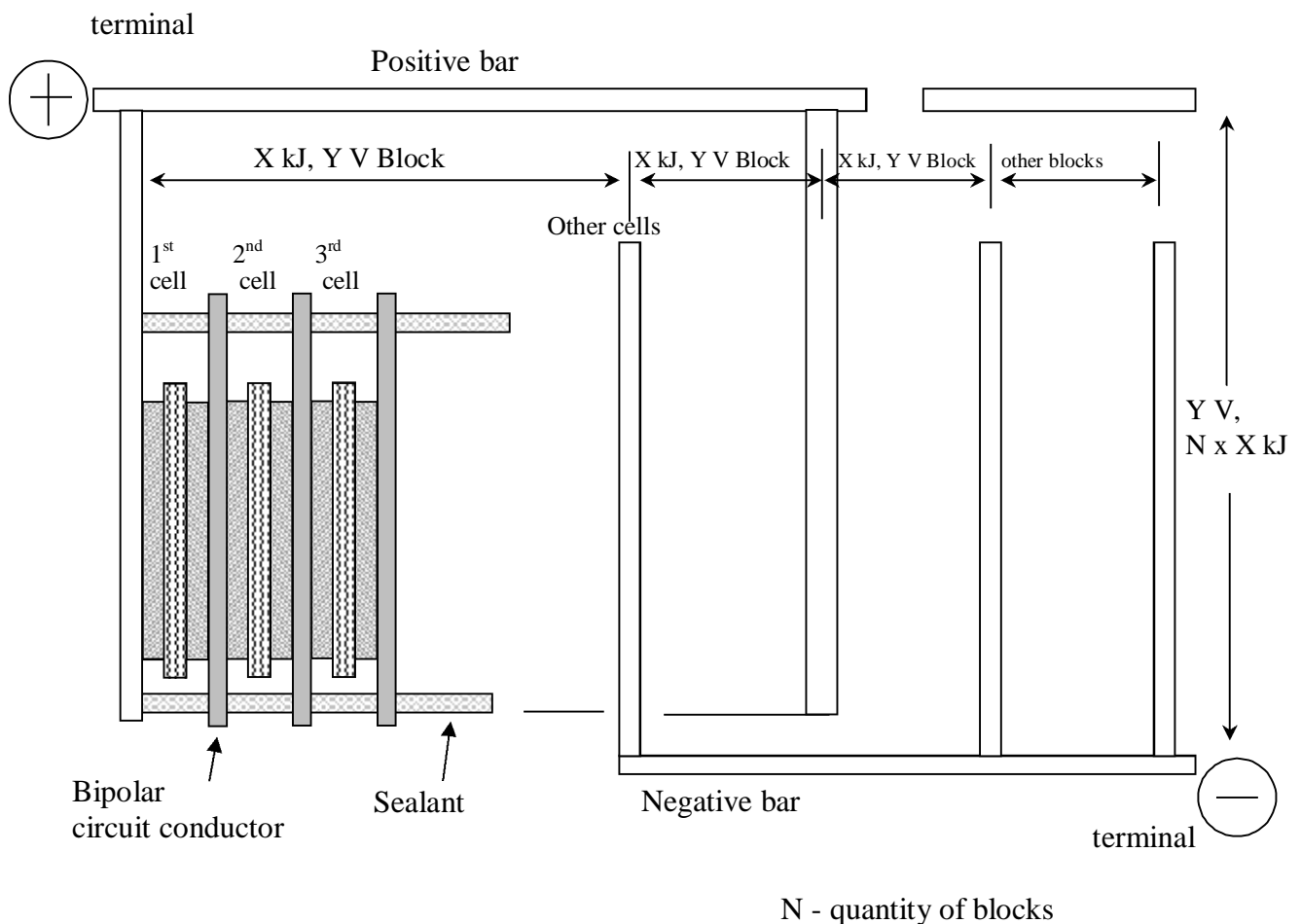


Fig. 1 Construction of starting SC

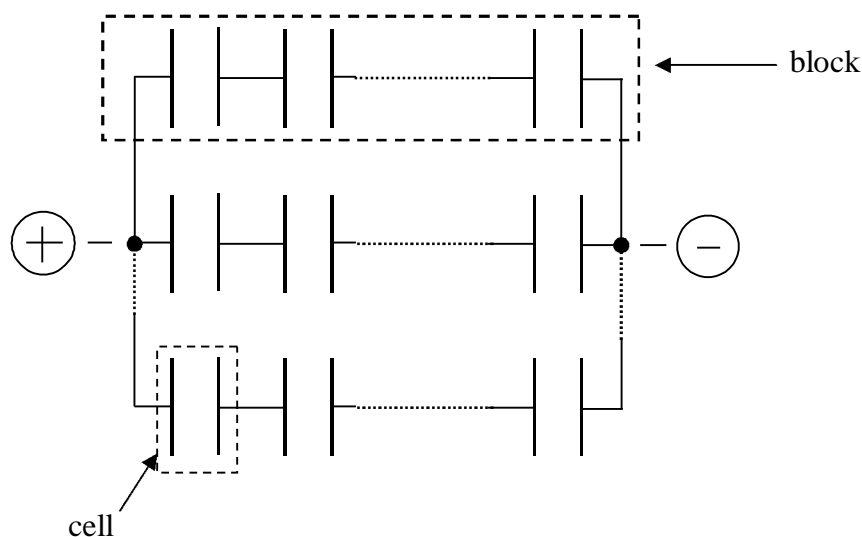


Fig. 2 Standard design and electrical commutation

The module consists of blocks of cells parallel connected for required energy store. Every block consists of cells series connected for necessary operating voltage.

Thickness of a single element is $<0,6$ mm. For commutation low resistant copper terminals with protective coat were used.

All the blocks are sealed and integrated into common vessel. From the sides they are fixed by covers and by the profile of electrodes they are separated from vessel by a polymer compound layer, being a damper and thermal insulation.

The parameters of typical samples of starting SC for cars and lorries are given in Table 3.

Table 3

PARAMETERS		VALUES, TYPES OF SCs							
1. Operating Voltage, average	(V)	12				24			
2. Energy Store	(kJ)	<u>5.8</u>	<u>6.9</u>	<u>8.3</u>	<u>9.1</u>	<u>37.4</u>	<u>44</u>	<u>51</u>	<u>54.6</u>
Initial Disch. Voltage	(V)	12	13	14	14.5	24	26	28	29
3. Internal Resistance,									
3.1. AC, 1 kHz	(Ohm)	0.003				0.003			
3.2. DC	(Ohm)	0.00029				0,00036			
4. Leakage Current /60 minute	(mA)	10				60			
5. Weight	(kg)	6,5				28			
6. Dimensions	(mm)	170 x 170 x 120				315 x 175 x 210			
7. Energy Density		<u>0.89</u>	<u>1.06</u>	<u>1.28</u>	<u>1.4</u>	<u>1.34</u>	<u>1.57</u>	<u>1.82</u>	<u>1.95</u>
		12	13	14	14.5	24	26	28	28
Initial Disch. Voltage		<u>1.67</u>	<u>1.98</u>	<u>2.29</u>	<u>2.62</u>	<u>3.23</u>	<u>3.8</u>	<u>4.4</u>	<u>4.7</u>
7.1. kJ/kg		12	12	14	14.5	24	26	28	29
7.2. kJ/lit									

5. Results Of SC Testing

In present item there're given typical, easily to be reproduced results of testing of starting SCs.

5.1. DC Discharge

The family of discharge curves of current 100 - 500 A is given in Appendix 1. In the graph the "sag" of the discharge curves, it's the lower, the higher discharge current is. The sag describes influence of charge distributed in volume and shows "non-ideal nature" of DLC in comparison with usual capacitors.

DC discharge of the system Battery+SC at temperature -20°C is shown in Appendix 2. Current - 200 A - is an average current of starter of cars Volga, GAZ-24. We gave therein comparative curves of commonly used battery 12 V, 60 Ah and of a new starting system - battery 12 V, 36 Ah and SC 12 V, 6 kJ. SOC of the battery is $\sim 40\%$. Increase of "effective" energy (hatched area) is clear in the initial phase of discharge. This phase is mostly important at cold cranking.

5.2. Engine Cranking By The System SC+Battery

During investigation we accumulated much of statistic material based on analyze of real curves of cranking and start of ICE. In Appendix 3. there're given typical oscilogrammes of cranking of ICE, 2,0 lit, at temperature -25°C . Starter 1.4 kW.

Usually to start ICE of such type a battery 60 Ah was used, in our system we used a battery 36 Ah. In condition of cold cranking with new battery the average starting frequency is ~ 165 rev/min, while the minimal required rate is just 90 RPM. It's an evidence of considerable reserve of power to produce guaranteed start.

5.3. Influence Of Temperature On Energy Output And Internal Resistance Of Starting SC

In the graphs of Appendixes 4, 5, 6. There're given the curves of dependence of output energy on load 0.04 Ohm, 1 Ohm and dependence of internal resistance upon temperature within window $-20^{\circ}\text{C} - +70^{\circ}\text{C}$. The data were obtained at testing on 3 modules 12 V, 6 kJ each, being differ in type of separator and in dozing of electrolyte. Considerable differences in energy output at SC discharge to load 1 Ohm and to load 0.04 Ohm, increasing at temperature decreasing, is well appreciable.

Summarising in brief the data of testing on SC and the system SC+ battery we can note the following:

- The efficiency of starting SC use in the system SC+ Battery is the higher, the lower SOC of battery and more severe start condition are:

- The rate of starter acceleration is higher and reduction the time of cranking to realise start is observed.

5.4. Service Life Testing By The Method Of Cycling

In present report I gave the data of testing of a single block, incorporated into module.

Its output data:

ESR - 19.8 m0hm;
capacity ~ 6 F.

The block was tested in the next regimes:

Charge: 5 sec to U_{oper} in regime U_{const} ;
Discharge: to load resistor < 0.01 Ohm, 3 sec;
Pause: 3 min.
After every 50 cycles -pause 30 min

The block was charged-discharged 150-200 times per 24 hours.

The data of the block after 150.000 cycles:

ESR- 22 mOhm:

Capacity- 6,3 F

Limit level:

ESR- not more 25 mOhm;

Capacity - not less 5 F.

The testing is being continued.

Thus, the bench mark testing show considerable reserve of service life, which exceeds one requested by vehicle manufacturers.

Besides ELIT Co. since 1990 has been carrying out road testing on different types of SC in cars and lorries.

5.5. Mechanical Effects

We carried out the next tests on standard module 24PP-30/0,003 <24 V,30 U>:

- Vibration in arises X, Y, Z with frequency 20-500 Hz, amplitude 6 g, during not less 30 hours in each axes;

- Single mechanical impact with peak acceleration 50 g;

- Repeated mechanical impacts with peak acceleration 15 g, 50 impacts/min in every axes, in total 600 impacts in each axes.

After the test the parameters of SC were not changed.

5.6. Some Data Of Comparative Testing Of SC With Aqueous And Non-Aqueous Electrolytes

One of the leading European Research Institutes carried out comparative testing on DLC with aqueous electrolyte (by ELIT Co.) and non-aqueous (by Panasonic) (Appendix 8).

Analysing the graphs we should not pay attention to the absolute value of energy, because that was testing on different types of capacitors. We must look at tends and spheres of exploitation. One can see the systems with non-aqueous electrolyte considerably (if compared with aqueous) decrease discharge efficiency at decreasing of temperature and increasing discharge current, and the DLC with aqueous electrolyte has more spheres of application.

6. Ways To Increase Specific Energy. Aspects Of DLC use to Hybrid Electrical drive

Analysing the data of specific parameters of DLC achieved and realised in industry, we can note their upper limit: ~2 U/kg and up to 5 kJ/tit when power and other parameters meet the requirements. Presently the level sufficiently satisfies the customers of the starting systems, nevertheless in the future this situation can be changed. Investigation being carried out during last time showed that high power DLC has a reserve to increase its specific energy.

Note: This time we scrutinize the ways to increase specific energy of DLC with water solution of electrolyte.

These are some of the ways to increase-specific energy:

- Share Reduction Of Passive Parts Of SC, which means optimization of design in order to lessen weight and volume of subsidiary parts (cover, case, terminals, separator). That gives principal increasing of specific energy to 10-15 %. Polarizable electrode must not be made thicker, it can lead to slowing down of energy output.

- Increasing Of Specific Surface Area Of Carbon in polarizable electrode should have directly increased capacity, but it's disputable, because aqueous electrolyte in some cases cannot

moisten the whole surface area and the phenomena requires additional investigation. On the other hand, increasing of specific surface area rises the cost of raw material.

- Increasing Of Operating Voltage Of A Single Cell is limited by destruction of solvent, (water) - 1.21 - 1.24 V. But in practice in serial manufacturing the operating voltage is 0.7 - 0.98 V. It's connected with natural technological distribute of parameters of assembled cells and possibility to achieve destruction voltage in some of the cells.

In some cases we can get a positive result if we use a shunt resistor of cell, which make the parameters of series circuit sufficiently equal thanked to exchange of leakage current.

No doubt, SC designers must go through all the above ways, nevertheless at our opinion achievement of considerable increasing of specific parameters is possible only by changing of electrode system of DLC.

So, in traditional conception of DLC there in 1 cell 2 single capacitors are allocated. These capacitors are in the same volume of electrolyte. It's sufficiently to take 1 capacitor away from the cell and the capacity will grow at least to 2 times. In order to obtain this, one of polarizable electrode must be changed with non-polarizable. Thus, we get a system with so called "ideal-non-polarizable" electrode. The best way is to use electrode with electrochemical reaction characterised by small value of polarization.

Taking into account the balance of capacity of the residual single capacitor and of non-polarizable electrode, the geometrical parameters (thickness) of the last one can be very small, because of its electrochemical capacity is considerably higher than of the residual polarizable electrode. That gives us additional improvement of specific parameters by volume.

It's desirable too the window of changing of the non-polarizable electrode potential to be as possible narrow during charge-discharge cycle. That make the diapason of operating potentials of polarizable electrode wider and increases cell capacity.

Detailed description of the system operation is out of the frame of present report, that's why the author stops at the said above. But additionally we must note that ELIT Co. During 1990-1991, having thoroughly investigated the system, we begun producing of so called "traction" SCs possessing specific parameters 2 - 2.5 times higher than of starting ones. In the traction SC an Nickel oxide electrode as an ideal non-polarizable, operating in the regime of proton exchange (charge-discharge) at potential lower than the potential of oxygen emitting was used (9).

The same system is a prototype to make a high power starting SC with energy store increased to 2-3 times.

As a result of R&D work being fulfilled by this time, ELIT Co. has got elements and blocks with parameters of a single cell.

The parameters are:

Operating voltage	(V)	1.15-1.19
Capacity	(F)	450-490
Full Energy	(J)	332
Internal Resistance, AC, 1 kHz	(Ohm)	0,0015
Weight	(g)	24
Volume	(cm ³)	12,32
Specific energy:	kJ/kg	13.5
	kJ/lit	26.2

Hybrid Electrical drive

It's widely known that energy capacitor based on DLC design is mostly suitable as accelerating - recuperative device for hybrid electrical drive (ICE-electro, electro-electro).

High available rate of charge-discharge, higher energy efficiency in comparison with chemical power sources at different level of energy store and maintenance free - these are characteristics belonging exclusively to DLC.

In different sources of information there're given different levels of absolute energy store, power, price. But we can note, that all the values are near about 5 Wh/kg (18 kJ/kg) and the value sufficiently meet requirements of electrical vehicles designers (10).

This level of specific energy is easily achievable by the system with 2 polarizable electrodes and aprotonic electrolyte. Doubt can be caused by the level of power which is connected with high specific internal resistance belonging to non-aqueous electrolytes. And at relatively high level of energy store the "effective" energy value will be at lower values of operating voltage. According to the data of " Auburn Capacitor" (10) specific power is 500 W/kg (1100 W/lit).

Possibly it demands additional measures from designers of electronic control devices for electrical vehicle.

Specific average power of starting SC with aqueous electrolyte being produced by ELIT Co. is following:

	Peak	100msec	500msec
by weight, W/kg	7000	3500	2500
by volume, W/lit	15000	7500	5000

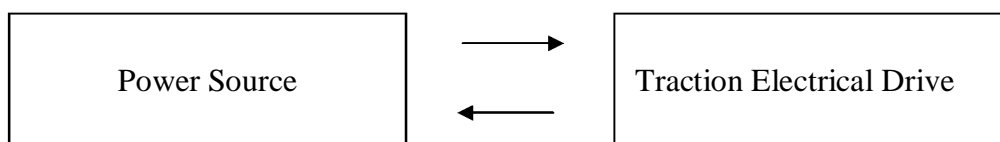
Now our task is just to increase specific energy and the possible ways to achieve that is to use the system with non- polarizable electrodes.

Basing on experimental data of advanced cell (see the beginning of this item) ELIT Co. carried out projecting of energy store set 120 V.

Calculated data are given below:

Operating voltage	(V)	120
Energy store	(kJ / Wh)	1056/293
Power	(kW)	>100
Internal resistance, AC, 1 kHz	(Ohm)	0,0045
Weight	(kg)	100
Volume	(lit)	55
Specific energy	kJ/kg / Wh/kg	10.56/2.93
	kJ/lit / Wh/Lit	19.2 / 5.33

Analysis of the above data shows very low level of ESR of the energy store set, which is not achievable by the non-aqueous electrolytes systems. And that means higher efficiency of energy transfer in the system:



Besides, higher (in comparison with non-aqueous electrolytes) energetic efficiency allows to use more effectively the energy being turned back to the power source at recuperative braking. In other words, the floating energy store of DLC with aqueous electrolyte is higher than of DLC with non-aqueous ones.

Summarising the above, we can make a conclusion that use of DLC with very low internal resistance as accelerating- recuperative block of hybrid electrical drive allows to reduce the absolute value of on-board energy store and the level of specific energy. That means that it's possible to use DLC with aqueous electrolyte and non-polarizable electrode to design a power source for hybrid electrical vehicle

e.g. Analyses of "driving" regime of SAE J227A of a vehicle with total weight 1000 kg shows "net" energy consumption ~490 kJ from power source. Taking into account the above parameters of the block 120 V, 1056 kJ and constant re-filling in energy by power source (ICE + generator, battery) there exist twofold energy store on vehicle board.

CONCLUSION

1. Complex of carried out investigations and results of testing on the DLC system with aqueous electrolyte allows to make a conclusion of expedient of their use as starting SCs. Relatively low level of specific energy (~2 kJ/kg) allows to put the SC under engine hood without prejudice to other power consumers and with increased guarantee of start.

2. The DLC systems with aqueous electrolyte and non-polarizable electrode (optimised variant) can be used as accelerating- recuperative device for hybrid vehicle. Lower level of specific energy in comparison with non-aqueous electrolytes, is compensated by high power of discharge and efficiency of recuperative recharge. Reducing of "absolute" on-board energy store and specific energy are allowable.

If to look at hypothetical future of common starting SCs use to start ICE and for hybrid electric vehicles, we can see the global ecological effect of DLC use, because using of SCs gives the opportunity to reduce relatively the on-board capacity of storage battery, the turning of lead and lead-based alloys, which were applied for starting battery production will be reduced in 2 times approximately.

And finally summarising all the above in the report, we can make the main conclusion:

At up-today level of DLC development and its industrial production we should not make universal capacitor with exotic parameters to solve at once all the problems of ICE start and of electric vehicle. Every type of DLC needs just technical adaptation and commercial analyses for a concrete type (family) of cars and electric vehicle with taking into account the specific character of exploitation. And while the further investigations in order to increase parameters of DLC are being carried out, different types of SCs can occupy their market niches right now.

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Enclosures:

Appendixes 1 - 8.