POWER PERFORMANCES OF HIGH ENERGY DENSITY CAPACITORS ON SYSTEM CARBON / NICKEL OXIDE

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Presented at The 9th International Seminar on Double Layer Capacitors
and Similar Energy Storage Devices.
Deerfield Beach, FL,
December 6-8, 1999

ABSTRACT

This work describes analyses of the processes in electrodes of combined capacitors of Carbon/Nickel Oxide system from the point of view of their influence on power. Typical makes produced in series were tested and evaluated. The testing program included discharge by DC, constant power, followed by analysis of discharge curves, measurements of potentials and estimation of electrode capacity. The analyzed data of pulse discharge within interval of 50 msec is given, as well. The capacitors of C/NiOx system with thick and thin electrodes are compared, and the system Carbon/Carbon.

Conclusion of this work is that operation of electrode in cell is non-proportional, the factor limiting energy output at higher power is the rate of electrode reaction in NiOx electrode. The advantages of use of thin NiOx electrodes at pulse discharge and power density equal and/or exceeding 5,000 W/kg are shown, too.

1. INTRODUCTION

Capacitors of the system Carbon/ Nickel Oxide show good properties being used as energy sources for electric vehicles with fixed route length (1, 2), since their specific energy is 10 Wh/kg and more, and power density is about 200 W/kg. High power capacitors of this system were developed as an additional unit for starting systems of combustion engines and for hybrid electric vehicles (3) during last years.

It is widely known that a cell of this system consists of a positive NiOx electrode with discharge processes of charge (proton) transmission and changing of level of oxidation $Ni^{2+} \leftrightarrow Ni^{3+}$. Negative carbon electrode possesses capacity discharge of double electric layer, and sometimes Faradaic process of hydrogen adsorption step. These electrodes operate in aqueous solution of potassium hydroxide.

The processes in NiOx electrode effecting on discharge power are described well enough during last 90 years, because this is a widely used electrode for Ni-Cad, Ni-MeH Storage Batteries. Using this electrode as a positive electrode in Carbon/NiOx system we can expect various polarization phenomena resulting in reaction rate and thus in power of a capacitor (4). Technological and electrochemical aspects of power relating to negative carbon electrode are well described, as well, at developing of powerful capacitor of the system Carbon/Carbon applied for starting systems of combustion engines (5). Nevertheless, aggregate electrode processes in combined capacitor of C/NiOx system and resulting in its power are described not sufficient, yet.

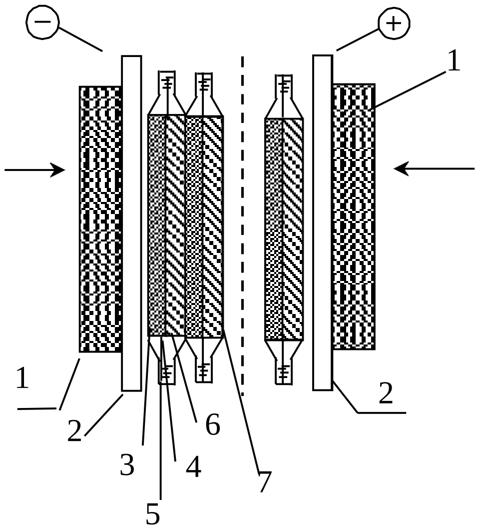
This paper is not to investigate a tested cell of this system by the potentio- and galvanostatic methods. Series product assembled with typical facilities for capacitors of carbon/carbon system were used for these tests, as well as typical testing methods for capacitors and storage batteries.

2. DESIGN AND FABRICATION

We manufactured blocks of 3 types, each with operating voltage of 21 V (for C/NiOx) and 15 V (for C/C) to estimate power profiles of C/NiOx system and to compare them with the system C/C.

2.1. Make of C/NiOx System

General view of the construction is in Fig. 1



1. Clumping Unit
2. Terminal (Cu/Ni)
3. Negative Electrode (C-pasted)
4. Separator (Paper)
5. Sealant - isolator
6. Positive Electrode (NiOOH-pasted)
7. Current Collector (Conductive plastic)

Fig. 1

Two blocks of this system differed from each other only in thickness of positive and negative electrodes (about two times). Needed dose of active material of positive electrodes was chosen to make its electrochemical capacity at least 3 times over the same of negative carbon electrode. Each cell of series circuit was made with precise pasting of active material mixed with KOH electrolyte onto proper collector made of conductive polymer of 26 microns thickness. After impregnation of separator with electrolyte and dosing, the collectors of positive and negative electrodes were sealed by welding through a dielectric spacer made specially for this. Some of cells were assembled in series to block, then added with nickel cover copper terminals. This block was clamped to required pressure in order to reduce contact resistance in a specially made clamping devise.

Authors considered minimization or cancellation of gassing in sealed cell in the end of charge or in the float mode under nominal voltage (2) to find optimum voltage for a cell. The value of 1.23 … 1.24 Volts per a cell appeared to be technologically acceptable.

2.2. Make of C/C System

We used typical capacitor block for level pick loads application in radio appliances. The block was bipolar. It was assembled under technology similar to one described in item 2.1. The difference in technology was that precise pasting of positive and negative electrodes was on different sides of conductive polymer collector. Sealed block was pressed in a clumping device to needed pressure.

2.3. Generalized Data of Makes of System C/NiOx and C/C (Table 1)

TABLE 1

Names of Parameters	C/NiOx, thick electrodes	C/NiOx thin electrodes	C/C
1. Capacity of block, F (discharge to load 10 Ohm)	29.5	11.69	17.42
2. ESR, Ohm	0.0567	0.0256	0.0178
3. RC-time constant, sec	1.68	0.3	0.31
4. Specific Energy kJ/kg (Wh/kg) kJ/Lit (Wh/Lit)	 12.3 (3.42) 18.9 (5.27)	 14.89 (4.13) 15.43 (4.29)	 4.83 (1.34) 6.29 (1.74)

Note: The data in the table above refer to block only, without terminals and clamping device.

3. RESULTS AND DISCUSSIONS

3.1. Discharge by DC

Here we shall comment the difference between the blocks with thin and the blocks with thick NiOx electrodes, and no compare with the system C/C.

General view on discharge curves of thick NiOx electrodes is in the Fig. 2, the initial steps are in Fig. 3. Analogue for thin electrodes, general view is in the Fig. 4, the initial steps are in Fig. 5.

Speaking generally, all the curves are of typical view on discharge capacity. Nevertheless, in case for thick electrodes there is seen slop of discharge curve in the part of voltage window from 0.6 to 0.7 Unom. This steepness depends directly on the value of discharge current. The authors analyzing this slop, and basing on the results obtained from experiments led earlier, came to conclusion that this dip was resulted by lower efficiency of charge-discharge processes in thicker lays of positive electrodes, comparing with efficiency in thinner lays. This is caused by increasing of Ohmic polarization in chain structures of pressed powder electrode as well as by kinetic polarization. Polarization is increased, too, if compare with thin lays due to enlarging convolution factor of the pores, appeared in porous structure of thick electrode.

Of course, it is possible to charge electrode considering overcharge by Ohmic and kinetic polarization. Nevertheless, this will initiate gassing (Oxygen) on positive electrode, which is not the task of this estimation described in this paper.

Influence of polarization difficulties in thick electrodes is clearly seen at estimation of output capacity vs discharge current (Fig. 6). We noted sharp dip of curve of capacity at increasing of discharge current. At the same time, thin lays show decreasing of capacity not so significantly, and this curve is more gently sloping.

3.2. Ragone Plot

To draw Ragone plot we used the data of discharge by DC with value multiplied by average value of discharge voltage. In the case of high level of power density, constant power discharge mode was used. If to look at Ragone plot at discharging of blocks to the voltage equal to half nominal, we can see that the curve of thick electrodes is in lower position than one of thin electrodes, though initial specific energy (Table. 1) is differ in 2 - 2.5 kJ/kg only. Besides, the shape of this curve is more steep if to compare with blocks with thin electrodes and the system C/C. It is easy to explain by increasing of polarization difficulties in voltage window 0.6 -0.7 Volt and drop of discharge curve (Fig. 3) in same window. Authors opinion is that it is impossibility of initial whole charge of NiOx electrode at given maximum values of charge voltage - 1.23 V.

If to draw Ragone plot with intervals between discharge voltages Unom $\rightarrow$ 0.7 Unom (i.e. to the point of inflection of discharge curve) (Fig. 8), then it is clearly seen that this make with thick electrodes has advantages over makes with thin electrodes to the point of Power density 750 W/kg.
Although the slop of this curve is more significant and the make with thin electrodes show same values of output energy and double power density: 3.6 kJ/kg at 2,750 W/kg versus 1,250 W/kg. Nevertheless there is a number of field of application where total decreasing of voltage as to 30 per cents of nominal is prohibited, and in this case the blocks with thick electrodes are preferable be used.

Note: the data of power in the above item relate to "Pure weight of block".

3.3. Process on Electrodes and Power.

To find out the factors limiting power of capacitors of C/NiOx system we tested and evaluated discharge performances of positive and negative electrodes of a number of separately given cells to be used for block assembling. We analyzed changing of voltage of each electrode of the cell and their individual capacity within window of operating voltage of a cell. These dependencies for cells with thin electrodes are in Fig. 9, same for the cell with thick electrodes is in Fig. 10.

These graphs show there were non-proportional operation of the electrodes in asymmetric C/NiOx cell:

- capacity of positive NiOx electrodes remains significantly higher (about 3 times) at lower current of discharge, than one of negative carbon electrodes at similar processes.
- At high discharge currents the capacity of negative carbon electrodes actually remains non-changed. At the same time capacity of positive NiOx electrodes gets lower significantly, and in some cases it is equal to the value of capacity of negative electrode (Fig. 9).

From the point of view of electrochemical processes on negative electrodes there is going a discharge of a double electric layer with slight effect of Faradic process. There is no significant polarization and decreasing capacity depends slightly on the value of discharge current. In some cases the capacity of negative electrodes at higher discharge currents can even be higher, than capacity at smaller currents. Kinetic polarization increases as well as Ohmic on positive NiOx electrode where Faradaic process is going with transmission of charge (proton).

Ohmic polarization is caused by contact resistance of electrode particles and by decreasing of conductivity of NiOOH grains during transition to the phase of discharge of $Ni(OH)_2$. Kinetic polarization is resulted by difficulties at activation of the reaction

$$NiOOH + H^+ \rightarrow Ni(OH)_2$$

Considering all the above we mark that capacity of asymmetric cell C/NiOx is controlled by capacity of NiOx electrode (rate of electrochemical processes) in the window of high discharge current. Thus, power is limited by positive electrode. Non-symmetry and non-proportionality of electrodes operation in cell both are more clear if to consider the case of discharge a cell with thick electrodes (Fig. 10). Capacity of NiOx electrode (~1000 F), at maximum value of discharge current 10 A, gets even lower than the capacity of negative electrode (~1,300 F), though at required quantity of active material it is 3 times higher than the capacity of negative electrode.

3.4. Pulsed Mode

To estimate power in pulsed mode we used other samples with construction analogues to described in the item "Design and Fabrication", with operating voltage 9 Volt. To compare the data we used the term "Current Efficiency of Capacity", i.e. discharge current divided by stored capacity. We chose the interval 1.5 … 1.92 A/F for all 3 samples. Discharge curves at this current load within interval 50 msec (Fig. 11) were compared. It is clear see that when current load A/F is similar, then the voltage value in the block with thin electrodes is 23 - 25 per cents higher than in the blocks with thick electrodes. But the main thing is that the block of the system C/C with thick electrodes possesses even higher level of voltage than a block of the system C/NiOx with 2 times thinner electrodes. This is one more confirmation of existence of polarization difficulties in kinetic of electrode reaction in NiOx electrode.

At the same time, the cells of C/NiOx system have higher technological voltage - 1.23 V per cell instead of 0.8 V as in the C/C system, and specific energy about 3 times higher. That is why we can expect gentle sloping of discharge curve within 50 msec interval at discharge by high power. Fig. 12 shows clear advantages of C/NiOx system with thin electrodes comparing them with C/NiOx and C/C systems with thick electrodes.

4. CONCLUSION

Results of estimation of power performances of C/NiOx system capacitor are as follow:

4.1. Insufficient charge of NiOx electrode of agglomerate construction (thick) results in decreasing of output energy at 0.6 … 0.7 of initial discharge voltage at limited level of charge voltage 1.23 V.

4.2. Authors noticed non-proportionality of positive and negative electrodes operation in a cell, and that technologically preset initial ratio of electrode capacities changes at increased charge current.

4.3. Energy output of the C/NiOx capacitor at high discharge power is limited by NiOx electrode (kinetic difficulties of electrode reaction)

4.4. Blocks of capacitors with thin agglomerate NiOx electrodes (< 100 micrometers) operate effectively at pulse discharge at high power density (5,000 W/kg).

ACKNOWLEDGMENTS

Authors thanks cordially Victor V. Melnik, Chief Engineer, JSC "ESMA, Moscow, Russia and Engineering-Testing Team of JSC "ESMA" for organization and leading of tests and evaluations of ELIT capacitors at high power density.

REFERENCES

1. A. Klementov, I. Varakin, , S. Litvinenko, N. Starodubtsev, A. Stepanov "Application of Ultracapacitors as Traction Energy Sources", Proceedings of "The 7th International Seminar on DLC and Similar Energy Storage Devices", December 8-10, 1997, Deerfield Beach , Florida, USA.

2. A. Beliakov and A. Brintsev "Development and application of combined capacitors: Double Electric Layer - Pseudocapacity" Proceedings of "The 7th International Seminar on DLC and Similar Energy Storage Devices", December 8-10, 1997, Deerfield Beach , Florida, USA.

3. A. Klementov, I. Varakin, S. Litvinenko, N. Starodubtsev, and A. Stepanov "New Ultracapacitors Developed by JSC ESMA For Various Applications", Proceedings of "The 8th International Seminar on DLC and Similar Energy Storage Devices", December 7-9, 1998, Deerfield Beach , Florida, USA.

4. B.E. Conway and W.G. Pell "Efficiency Aspects of Charge/Discharge Cycling at porous capacitor Electrodes: Behavior of a Hardware Model Circuit", Proceedings of "The 8th International Seminar on DLC and Similar Energy Storage Devices", December 7-9, 1998, Deerfield Beach , Florida, USA.

5. A.I. Beliakov "Investigation and Development of DLC for Start of Internal Combustion Engines and of Accelerating Systems of Hybrid Electric Drive", Proceedings of "The 6th International Seminar on DLC and Similar Energy Storage Devices", December 9-11, 1996, Deerfield Beach , Florida, USA.

Appendixes: Fig. 2 - Fig. 12