ELECTROCHEMICAL SUPERCAPACITOR TIME DOMAIN ANALYSIS BY MEANS OF MULTI-CHANNEL MEASUREMENT SYSTEM

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Abstract-In this paper we present the multi-channel measurement system based on potentiostatic, galvanostatic and potentiodynamic methods or combinations of the given measurement methods. The multi-channel measurement system is controlled with the special developed software. This system enables to perform the electrochemical supercapacitor time domain analysis more completely and with high accuracy.

I. Introduction

For electrochemical supercapacitors quality control the manufacturers use the simple sampling inspection method, which consists of the three basic tests: the capacitance test, the alternative current electric serial resistant (AC-ESR) test and the self-discharge test [1]. While carrying out these tests the electrochemical supercapacitor is charged to rated voltage at first and then its capacitance is measured in galvanostatic discharge mode by means of the constant current source J=const during of time Δt. In this case capacitance is defined by a well-known equation (1).

$$C = \frac{J\Delta t}{\Delta u}, \tag{1}$$

where Δu is the electrochemical supercapacitor voltage drop.

The AC-ESR test is performed by means of 4-probe impedance analyzer in the potentiostatic mode with AC voltage amplitude of 4mV at frequency of 1 kHz. And finally, the self-discharge test includes the electrochemical supercapacitor open circuit voltage (OCV) measurements with two stages: at first, the supercapacitor is charged to rated voltage and then OCV is measured after 1hrs.
The main disadvantage of the simple sampling inspection method is the simple linear electrochemical supercapacitor equivalent circuit which includes only three elements: capacitance C, ESR R and self-discharge resistance R_{SD} as shown in Figure 1.

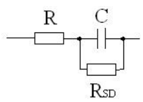


Figure 1. Simple linear electrochemical supercapacitor equivalent circuit

The conducted researches [2,3] show that the simple linear electrochemical supercapacitor equivalent circuit cannot describe the real behavior of supercapacitors at wide current, voltage and frequency ranges that are used in real applications. Capacitance, AC-ESR and self-discharge depend on measurement conditions such as charge-discharge current, voltage and frequency of applied measurement signal. For example, capacitance of the electrochemical supercapacitor (5 Farad, 2.3 Volts) manufactured by Ness Capacitor Co., Ltd (South Korea) differs more than two times when measurements are conducted with discharging currents 5mA and 1.8A as shown in Table 1.

Capacitance values of the electrochemical supercapacitor 5F at rated voltage 2.3V Table 1

Charge mode		Discharge mode	
Current, mA	Capacitance, F	Current, mA	Capacitance, F
5	7.48	5	5.88
90	5.1	90	5.2
1800	3.9	1800	3.25

Capacitance and AC-ESR measured for the same electrochemical supercapacitor by alternative current vary at frequency range of 0.1 mHz to 10 Hz as shown in Figure 2.

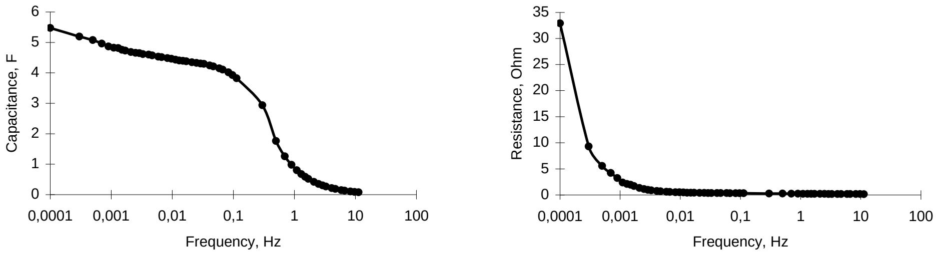


Figure 2. Capacitance and AC-ESR vs. frequency

By analyzing given experimental results we can make conclusion that it is necessary to use more complicated non-linear electrochemical supercapacitor equivalent circuit for determining their electrical characteristics. On the other hand, the simple sampling inspection method is not accurate enough because the electrochemical supercapacitor electrical characteristics are more complicated than capacitance, AC-ESR and self-discharge resistance.

II. Principle of the multi-channel electrochemical supercapacitor measurement system

The main principle of the multi-channel electrochemical supercapacitor measurement system is a variety of measurement modes combined with their high accuracy and automatic operation under personal computer control. The multi-channel measurement system block diagram is shown in Figure 3.

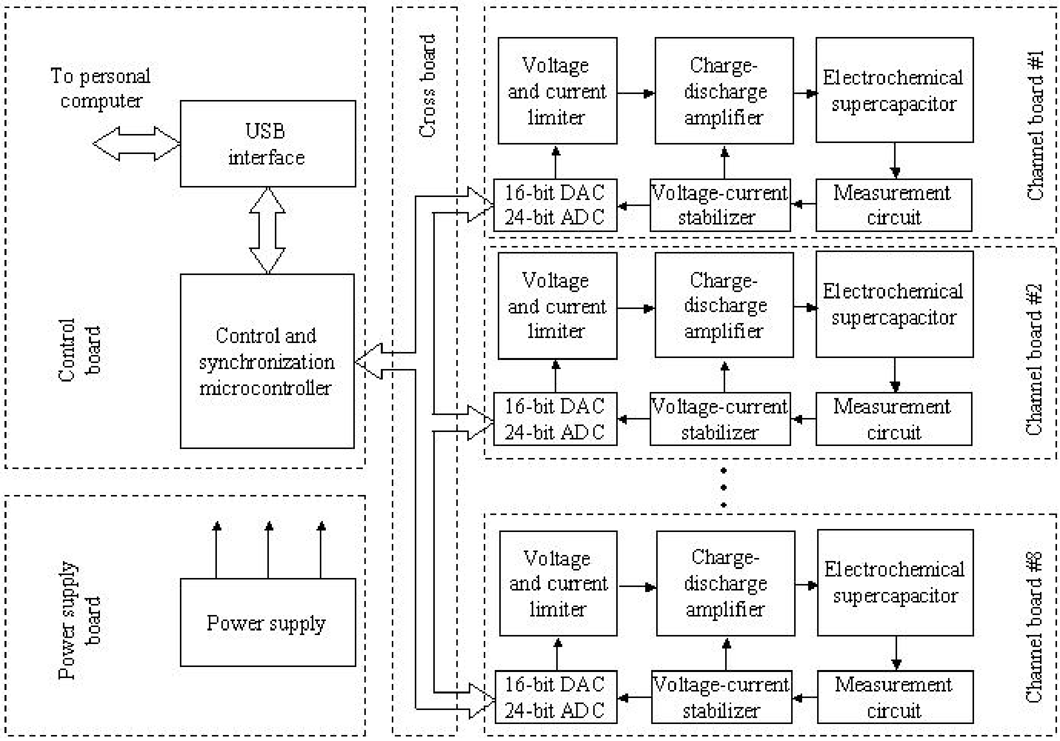


Figure 3. Multi-channel electrochemical supercapacitor measurement system block diagram

The multi-channel electrochemical supercapacitor measurement system consists of 8 independent measurement channels that are designed as 8 channel boards. Channel boards are connected to a control board that includes the microcontroller and USB interface for connection to computer as shown in Figure 4.

Technical specifications

Operating modes:

Galvanostatic - constant current (current ranges 1, 10, 100 and 2000mA)
Potentiostatic - constant voltage (voltage range from -10V to +10V)
Potentiodynamic - linear voltage changing (max speed 100mV/sec)
Combined - charge/discharge in galvanostatic mode and supporting potential in potentiostatic mode to obtain the set leakage current

Measurement accuracy:

Current - ±0.2%
Voltage - ±0.1mV
Sampling period - 1msec
ADC - 24bits
DAC - 16bits

Figure 4. Multi-channel electrochemical supercapacitor measurement system

The system allows expanding the number of channels to sixteen. Both hardware and software can be modified to the 16 independent channels by means of adding the 8 additional channel boards. The software of the multi-channel electrochemical supercapacitor measurement system consists of three programs. The first one is the microcontroller program that operates inside of microcontroller as shown in Figure 5.

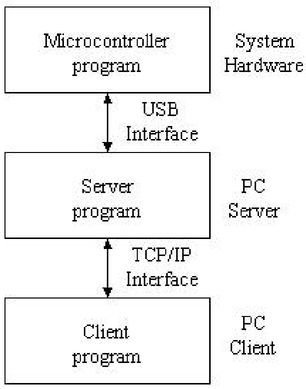
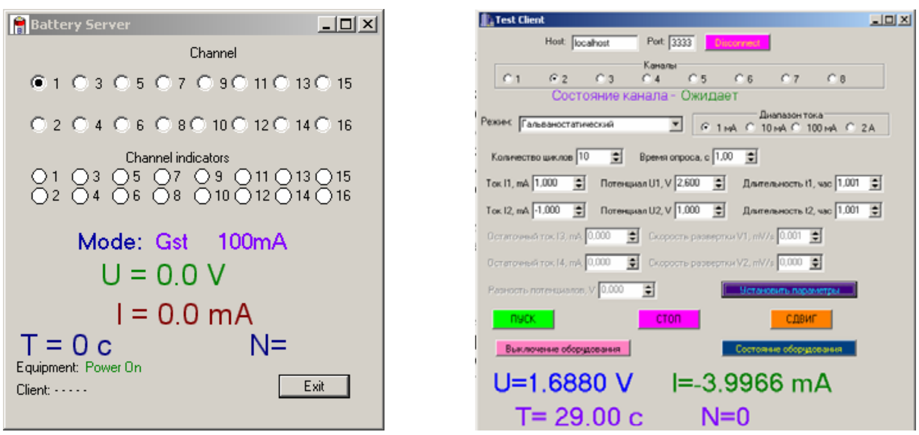


Figure 5. Software components of the multi-channel electrochemical supercapacitor measurement system

The next program is the server program that allows controlling many users through the client programs of independent cannels. Every channel is fully independent and can be controlled by one user. The user interface of the server program is shown in Figure 6 (a). As shown in Figure 5 the system hardware communicates to the PC server through the USB interface. The PC clients can be in different rooms and communicate to the PC server through the TCP/IP interface using Internet. The user interface of the server program is shown in Figure 6 (b).



(a) (b)

Figure 6. User interface of the server and client programs

By means of the remote access to the multi-channel electrochemical supercapacitor measurement system through the client PC the customer controls data acquisition process using Internet. It is very useful for the long data acquisition processes. In this case the customer can treat the obtained data without direct contact to the multi-channel electrochemical supercapacitor measurement system.
The multi-channel electrochemical supercapacitor measurement system can operate in fully automatic or half automatic modes. In the fully automatic mode the system performs the measurement process without additional control signals. All received data are saved to the PC hard disc into the separated data files without additional treatment.

III. Methodology

According to circuit theory, the electrochemical supercapacitor equivalent circuit in galvanostatic charge mode is shown Figure 7.

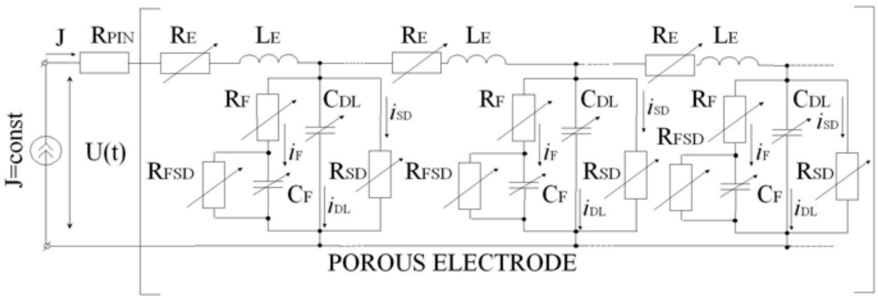


Figure 7. The electrochemical supercapacitor equivalent circuit for galvanostatic charge mode

In this equivalent circuit: R_{PIN} is the pin resistance; R_E is the non-linear distributed electrode resistance; L_E is the parasitic distributed electrode inductance; R_F is the non-linear distributed Faradaic resistance; C_{DL} is the non-linear distributed double-layer capacitance; C_F is the non-linear distributed Faradaic capacitance; R_{FSD} and R_{SD} are the non-linear distributed Faradaic and non-Faradaic self-discharge resistances respectively.

The current J is divided into three distributed currents: $i_F = C_F \frac{\partial U_F}{\partial t}$ is the distributed Faradaic current; $i_{DL} = C_{DL} \frac{\partial U_{DL}}{\partial t}$ is the distributed double-layer current; and i_{SD} is the distributed self-discharge current. These currents are distributed along the electrochemical supercapacitor porous electrode with the length *l*.
Therefore,

$$J = \int \left(i_F + i_{DL} + i_{SD} \right) dl \tag{2}$$

The voltage U(t) is determined by expression:

$$U(t) = JR_{PIN} + U_{PE}(t)\,, \tag{3}$$

where $U_{PE}(t)$ is a voltage of the electrochemical supercapacitor porous electrode.

In this expression the electrochemical supercapacitor porous electrode voltage $U_{PE}(t)$ is defined by equation (4):

$$U_{PE}(t) = \frac{1}{C_{PE}} \int J dt = \frac{1}{C_{PE}} \int \left(\int (i_F + i_{DL} + i_{SD}) dl \right) dt\,, \tag{4}$$

where C_{PE} is the equivalent non-linear capacitance of the electrochemical supercapacitor porous electrode that is measured at constant currents *J* as shown in Table 1 above.

IV. Experimental

The experimental researches were performed with our multi-channel electrochemical supercapacitor measurement system for 16 commercial samples of the electrochemical supercapacitors (model

HP0005-0023B with a nominal 5 Farad and a rated voltage 2.3 Volt) manufactured by Ness Capacitor Co., Ltd (South Korea). These results are shown in Table 2.

Charge/Discharge Tests of the 5F 2.3V NESS Supercapacitors Table 2

Samples	Constant Load R=1.5Ohm			Constant Voltage Charge V=2.3V		Constant Voltage Discharge V=2.3V		Relaxation voltage	
	I_{max}, mA	T=20s		T=20s	Tran. Time, sec	T=20s	Tran. Time, sec	V_{min} V	V_{max} V
		V, V	I, mA	I, mA		I, mA			
#1	692.1	0.117	73.21	252.3	5	81.43	4	0	0
#2	922.68	0.18	118.91	26.53	5	19.35	5	1.47	0.38
#3	986.76	0.18	118.24	44.06	5	22.58	5	1.32	0.52
#4	1053.7	0.16	104.98	32.74	6	20.15	5	1.46	0.64
#5	1330.46	0.26	169.97	22.94	7	26.35	6	1.83	0.29
#6	1061.55	0.18	113.86	30.67	5	21.18	5	1.6	0.42
#7	1009.33	0.17	114.04	30.30	5	18.38	4	1.59	0.58
#8	922.68	0.16	104.3	32.74	6	20.21	6	1.53	0.53
#9	1237.42	0.18	118.61	29.94	6	16.92	4	1.45	0.45
#10	1021.14	0.18	111.79	34.02	5	24.59	5	1.41	0.39
#11	1070.67	0.19	123.48	35.35	4	24.89	4	1.54	0.55
#12	944.77	0.15	92.87	33.71	6	17.71	4	1.5	0.55
#13	1342.63	0.26	174.59	28.17	6	20.08	5	1.76	0.44
#14	1209.42	0.26	165.16	22.76	7	16.56	6	1.66	0.21
#15	707.74	0.13	84.04	82.21	4	54.77	4	1.21	0.68
#16	1154.84	0.23	153.9	37.42	5	25.01	6	1.57	0.47

As shown in Table 2, the samples #5, #13, #14 and #16 have much higher maximum discharge current for the same value of resistive load. Comparing to other samples which have the same capacitance values of 5F they can support much higher values of voltage and current on the resistive load during the same period of time T=20sec. There is also a very big deference between the relaxation charge/discharge voltages for these four samples. But manufacturer who uses simple inspection method for sample measurements doesn't identify the above mentioned differences in technical specifications for all samples. It is a main disadvantage of simple inspection method.

V. Conclusions

The phenomenon of capacitance dependence on measurement current values is explained by a complicated physical and chemical nature of the electrochemical supercapacitor charge storage. The non-linear equivalent capacitance of the electrochemical supercapacitor porous electrode includes non-linear distributed double-layer capacitance and non-linear distributed Faradaic capacitance. These two capacitances have different time constants. Therefore, if the electrochemical supercapacitor is charged with high current the non-linear distributed double-layer capacitance is charged to a rated voltage faster than non-linear distributed Faradaic capacitance.

The developed multi-channel electrochemical supercapacitor measurement system together with special software allows to research the electrochemical supercapacitor in the time domain more accurate and automatically. This system can be very helpful for the researches another electrochemical current sources like battery or fuel cells also.

References

[1] B.E. Conway, Electrochemical Supercapacitors: Scientific Principles and Technological Application, Plenum, New York, NY, 1999.

[2] V. Martynyuk, O. Vdovin, J. Boyko and N. Vlasenko, “Super-High Capacitor Analyzer with Compensation of Common-Mode Error”, Proc. of the 11th IMEKO TC-4 Symposium “Trends in electrical measurement and instrumentation”, Lisbon, Portugal, pp. 340-343, 2001.

[3] O. Vdovin, V. Martynyuk, M. Surdu, “A Combined Method for Measuring Super-High Capacitor Absorption Characteristics”, Proc. of the 11th IMEKO TC-4 Symposium “Trends in electrical measurement and instrumentation”, Lisbon, Portugal, pp. 373-375, 2001.