Charge Redistribution and Restoring voltage of Supercapacitors

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Abstract:
Electric charge in supercapacitor is stored on electrodes as well as inside its electrolyte. Charges on electrodes create Helmholtz double layer which is formed immediately with time constant in the order of seconds, while the storage of charge in electrolyte takes time in the order of hundreds of seconds. When the charged supercapacitor is briefly short-circuited, the charge on electrodes is discharged, however the charge in electrolyte remains mostly unchanged. The charge stored in electrolyte is redistributed by diffusion to the electrodes, until the charge on electrodes form electric field which acts against the charge concentration gradient and equilibrium state occursfor charge-carrier exchange at electrode/electrolyte interface. Supercapacitor capacitance value depends on the voltage of its terminals; with increasing voltage total capacitance increases.

INTRODUCTION

Supercapacitor (SC) is an electronic device able to store large amount of energy within relatively short time period. Due to high capacity (in thousands of Farads) SCs could be used as an extra power source. The detail study of SCs charge and self-discharge processes were performed in [1], [2], [3], [4], [5], [6] and [7].
The charge on SC with carbon electrodes is stored not only in Helmholtz double layer on the interface between a conductive electrode and an electrolyte but also in the electrolyte itself. Helmholtz capacitance is charged immediately with time constant in the order of seconds, while the charge stored in electrolyte is redistributed by diffusion process, which leads to the increase of total capacitance of the sample. This diffuse capacitance is charged with time constant in the order of hundreds of seconds [5]. The increase of capacitance due to the charging of diffuse capacitance leads to decrease in potential on SCs terminals.
We describe mathematical method for obtaining accurate estimation of capacitance vs. voltage relation of tested SC. We show how to extrapolate this information from charging and discharging characteristics of SC. In the process we estimate SCs immediate capacitance and constant, which characterize SCs capacitance in relation to the voltage on its terminals. We show how to estimate SCs differential capacitance. We calculate equivalent capacitance of linear capacitor holding the same charge, and the same energy, respectively, as the evaluated SC [8].
We have prepared an experiment where the SC is charged for time interval of 600 seconds from the voltage source through the load resistor up to reaching the operating voltage. We can calculate total charge delivered to SC within this time interval. After this charging interval the capacitor is shorted for 12 seconds, in which the entire charge from electrodes is discharged. Charge stored in the electrolyte is then slowly redistributed and the voltage on SC terminals increases. We have monitored this restoring voltage value in time interval of 4000 seconds. The time dependence of restoring voltage can be modeled by the exponential stretched law, which shows, that the charge redistribution is driven by diffusion process.

CAPACITANCE DEPENDENCE ON ELECTRIC FIELD

As mentioned above, the physics of the SC predicts a voltage dependent value of capacitance. We identify the capacitance from the voltage vs. time curve during the charging (Fig. 1:) or discharging (Fig. 2:) by constant current I_C.

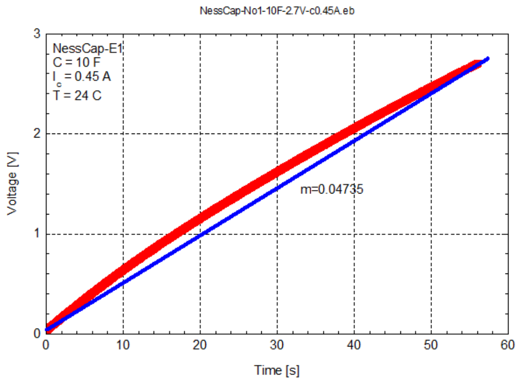

Fig. 1: Voltage vs. time for SC Nesscap 10F/2.7V during charging by constant current (blue line represents linear approximation).

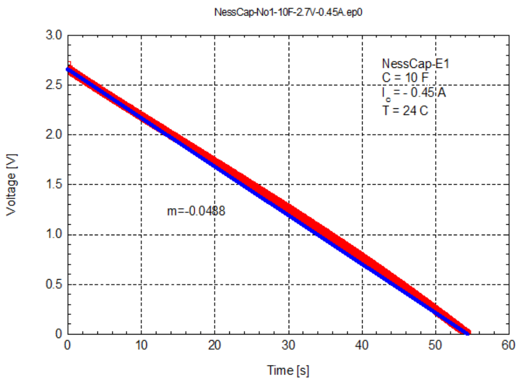

Fig. 2: Voltage vs. time for SC Nesscap 10F/2.7V during discharging by constant current (blue line represents linear approximation).

Electric charge stored on SC during charging can be calculated as $Q = I_C * t$, where t is time of charging. Stored electric charge vs. voltage dependence is determined from SC charging and can be approximated by 2nd order polynomial function [6] (see Fig. 3:):

$$Q = C_{H0} V + 12 C_{H1} V^2 \quad . \qquad (1)$$

Where C_{H0} is Helmholtz or immediate capacitance and C_{H1} is constant which characterize voltage dependence of SC capacitance.

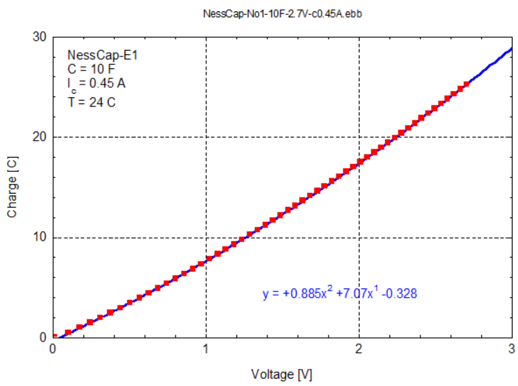

Fig. 3: Stored electric charge vs. voltage for SC Nesscap 10F/2.7V for charging by constant current I_C = 0,45 A

From the curve fit obtained from Fig. 3: it follows that for SC Nesscap 10F/2.7V the capacitance values during charging were roughly C_{H0} = 7.07 F and C_{H1} = 1.77 F/V.

Differential capacitance C_δ is given by the first derivative of stored charge Q vs. applied voltage V:

$$C_\delta = dQdV \quad , \qquad (2)$$

hence from equations (1) and (2) we get:

$$C_{\delta} = C_{H0} + C_{H1} V \quad . \qquad (3)$$

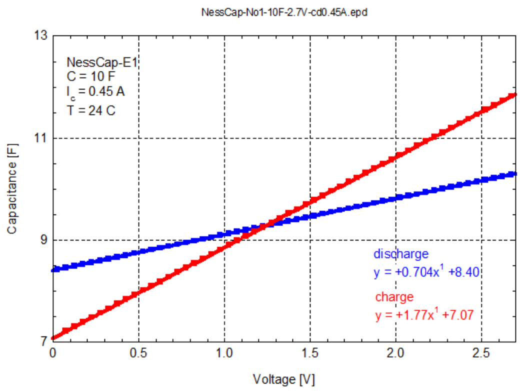

Fig. 4: Capacitance vs. applied voltage for Nesscap 10F/2.7V for charging/discharging by constant current I_C = 0,45 A

Capacitance depends on voltage. With increasing voltage the capacitance increases both for capacitor charging and discharging process as shown in Fig. 4:.
Two different capacitance values are defined [8] by following terms:
The first one is the equivalent capacitance defined as capacitance value of a linear capacitor holding the same charge as the SC at the voltage *V*. This capacitance is denoted by C_{HQ} and is obtained from (2) and (3):

$$C_{HQ} = C_{H0} + 12 C_{H1} V \quad , \qquad (4)$$

where *V* is voltage on the SC after the charging. C_{HQ} corresponds to average value of SC capacitance and it is very near to the nominal capacitance value for rated voltage.
The second one is the equivalent capacitance C_E defined as the capacitance of linear capacitor having the same energy *E* as the SC at the voltage *V*. Energy stored in generic capacitor is given by following equation.

$$E = \int V \, dQ \qquad (5)$$

Energy of linear capacitor is obtained by integration of (5), introducing the relation $dQ = C_E \, dV$,

$$E = \frac{1}{2} C_E V^2 \quad . \qquad (6)$$

Energy stored in SC is calculated by combining equations (2), (3) and (5) such as:

$$E = \frac{1}{2} C_{H0} V^2 + \frac{1}{3} C_{H1} V^3 \quad . \qquad (7)$$

This nonlinear behavior of the immediate capacitance of the SC has the consequence that more energy per voltage increment is stored at higher voltage than it would be in a constant linear capacitor. The equivalent capacitance C_E is given by equaling equations (6) and (7):

$$C_E = C_{H0} + 23 C_{H1} V \quad . \qquad (8)$$

The explanation of SC voltage-dependent capacitance follows from electric charge distribution in SC active region. The distance between positive and negative electric charges is constant in parallel plate capacitor. In SC this distance is dependent on the value of electric field in time because of the charge carriers' movement.

EXPERIMENTAL

The samples of SC Nesscap 10F/2.7V were evaluated [7]. SC in series with load resistance was connected to the DC power source for time interval of 600 seconds. Voltage on SC's terminals and charging current were recorded with sampling frequency of 20 Hz. Acquired characteristics are shown in Fig. 5:.

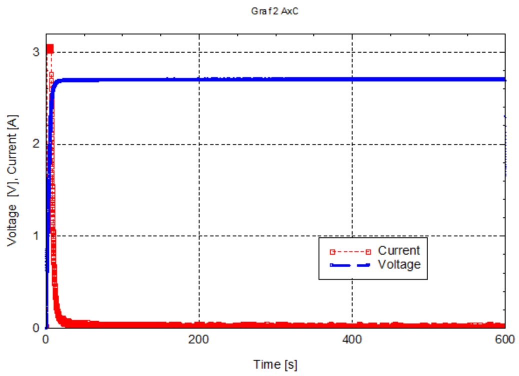

Fig. 5: Time dependence of voltage on SC's terminals (blue curve) and charging current (red curve) during charging of SC Nesscap 10F/2.7V – whole charging time interval 600 seconds.

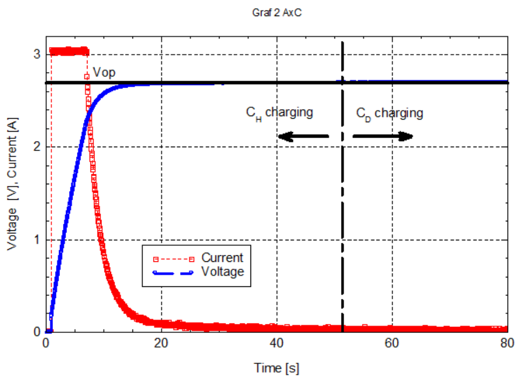

Fig. 6: Detail of initial 80 seconds of Fig. 5:

Operating voltage (V_{op}) value 2.7 V is reached within the time interval of 50 seconds and then the voltage is kept at constant value (see Fig. 6:). The charge delivered to SC was calculated by integrating the charging current in the time interval 0 to 50 seconds, and 0 to 600 seconds, respectively. The charge delivered to SC within initial 50 seconds is Q_{50s} = 27.5 C, and the total charge of SC after 600 seconds of charging is Q_T = 32.08 C.
After the charging of SC for 600 seconds the SC was discharged through the shunt resistor R_{L2} = 0.25 □. Time dependence of discharge current and voltage on terminals is shown in Fig. 7: and Fig. 8:. The voltage on SCs terminals reached zero value within 12.5 seconds. The charge taken out from SC was calculated to be Q_{dis} = 27.4 C.

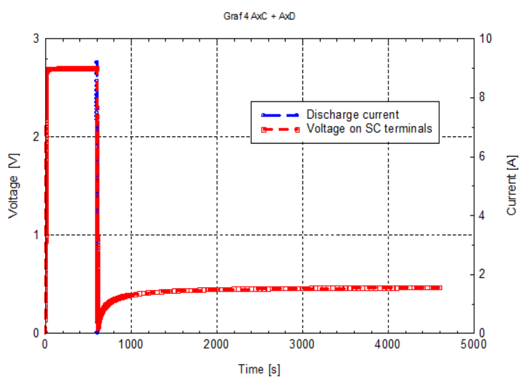

Fig. 7: Time dependence of discharging current (blue curve – time interval 602 to 614 s) and voltage on SC's terminals (red curve) during charging, discharging and voltage recovery on SC Nesscap 10F/2.7V.

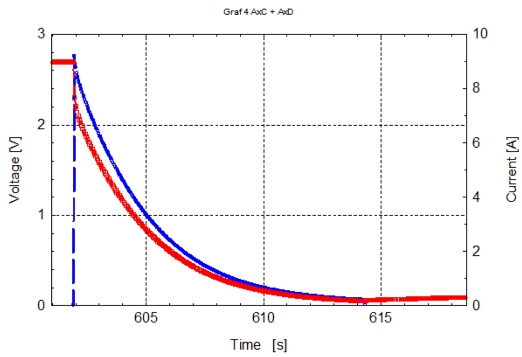

Fig. 8: Time dependence of discharging current (blue curve – time interval 602 to 614 s) and voltage on SC's terminals (red curve) during discharging of SC Nesscap 10F/2.7V – detail for time interval 601 to 619 s.

From our previous experiments on SC Nesscap [5] it follows that we can neglect the charge losses due to the current leakage. The leakage current is in the order of 1 to 10 µA, so the charge loss is less than 50 mC during the whole experiment.

DISCUSSION

From the comparison of Q_{50s} and Q_{dis} charge values it follows, that during initial 50 seconds of charging, the charge is stored mostly on the SCs electrodes. Then during additional 550 seconds of charging, the charges are stored in electrolyte. The time dependence of charging current in time interval 50 to 600 seconds can be approximated by analytical function (see Fig. 9) where the charging current exponentially decreases with square root of time, which corresponds to the charge redistribution by diffusion process:

$$I = I_1 \cdot \exp\left(-\sqrt{t/\tau}\right) + I_2 \,, \qquad (9)$$

where I_1 = 0.0309 A, t is time, time constant τ = 44.6 s and I_2 = 0.0072 A.
Here I_1 + I_2 = 0.0381 A is the current value in time 50 seconds. Value of current I_2 represents the value at infinity, but it is not equal to the SCs leakage current, which is in the order of 1 to 10 µA in these components [5]. Measured value of current I_2 is about 3 orders of magnitude higher than expected leakage current value, which shows that the charge diffusion is still in progress and that more charges could be stored in electrolyte.

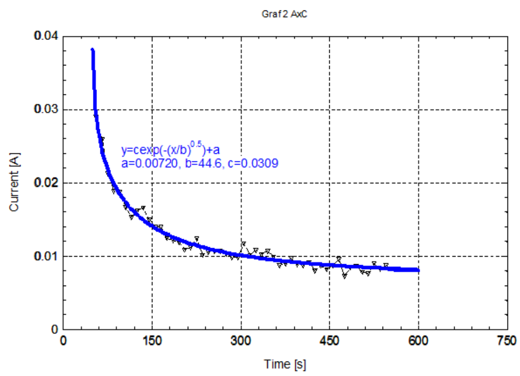

Fig. 9: Time dependence of charging current (black curve) during charging of SC Nesscap 10F/2.7V in time interval 50 to 600 seconds and the data fit by analytical function (blue line).

Total charge stored in the SC during charging was Q_T = 32.08 C. Voltage on SC's terminals was kept at operating value V_{op} = 2.695 V. Considering the amount of charge stored on electrodes to be equal to Q_{dis} = 27.4 C, then the charge stored in electrolyte during 600 seconds of charging is $Q_E = Q_T - Q_{dis}$ = 4.68 C.
We can calculate the Helmholtz capacitance as $C_H = Q_{dis} / V_{op}$ = 27.4 / 2.695 = 10.17 F and the total capacitance after 600 s of charging $C_{T6000s} = Q_T / V_{op}$ = 32.08 / 2.695 = 11.90 F.
When the SC is shorted all charge from electrodes is discharged. Charge stored in the electrolyte Q_E is then redistributed and the voltage on SCs terminals increases (see Fig. 10:). The time dependence of restoring voltage can be modeled by exponential stretched law, which shows that the charge redistribution is driven by diffusion process. The analytical function for restoring voltage fit is:

$$V_r = V_{r1}(1 - \exp(-\sqrt{t/\tau})) \quad , \qquad (10)$$

where V_{r1} = 0.461 V is the restoring voltage value at infinity and the time constant is = 104 s.
From the charge QE remaining in SC and the restoring voltage value Vr1 we can calculate total capacitance for voltage 0.461 V as $C_{TVr} = Q_E / V_{r1}$ = 4.68 / 0.461 = 10.15 F.
We can see that the value of capacitance C_{TVr} is smaller than the Helmholtz capacitance value at V_{op}. Capacitance of SC is voltage dependent and at least Helmholtz capacitance value increases with voltage on its terminals.

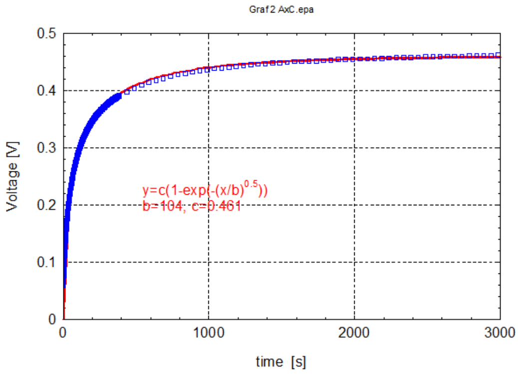

Fig. 10: Time dependence of voltage on SC's terminals (blue squares) during the voltage recovery after the SC short ciurcuit for SC Nesscap 10F/2.7V. Here time t = 0 s corresponds to the point t = 614.25 s in Figs. 7 and 8.

CONCLUSIONS

The electric charge on SC with carbon electrodes is stored not only in Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte, but also in the electrolyte itself.
The charges on electrodes create Helmholtz double layer, which is formed immediately with time constant in the order of seconds.
The charge storage in electrolyte (diffuse capacitance) is going on with time constant in the order of hundreds of seconds and the charge redistribution in SC structure is described by diffusion process.
When short-circuiting the SC for short period of time the potential of its terminals reach zero. The restoring voltage on SCs terminals increase within time interval of thousands of seconds.
Capacitance of SC is voltage dependent and at least Helmholtz capacitance value increases with voltage on the SC's terminals. The immediate capacitance of SC and its voltage dependence factor can be accurately estimated. And an equivalent capacitance of linear capacitor can be calculated.

ACKNOWLEDGMENTS

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