

Supercapacitors investigations

Part I: Charge/discharge cycling

I – INTRODUCTION

Among all the systems dedicated to energy storage, supercapacitors are one of the most promising, especially for powering electronic devices. This application requires an energy storage device able to provide many charges/discharges and short term pulses (a typical shape of current pulses is displayed in Fig. 1). These requirements are in agreement with the intrinsic characteristics of the supercapacitor.

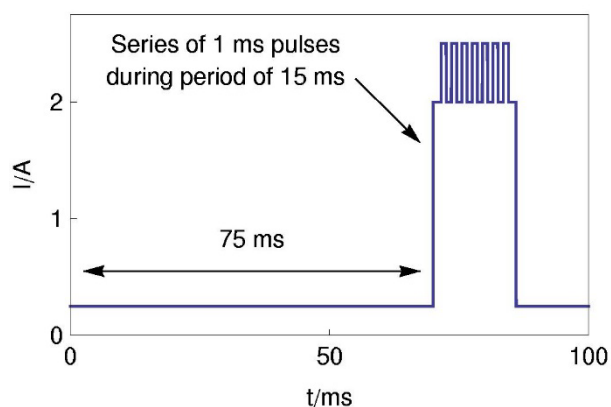


Figure 1: Typical pulse output requirement for a digital communication device from ref [1].

The capacitor is made of one anode and one cathode separated by a dielectric membrane (Fig. 2). The capacitor is called a supercapacitor when the capacity is higher than 1 F

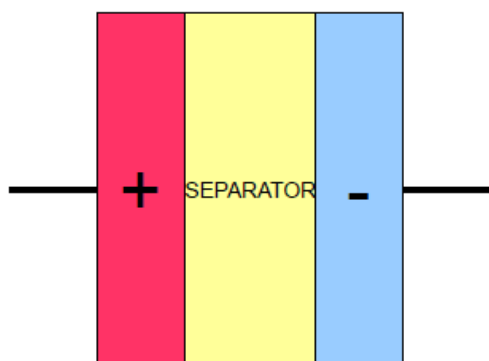


Figure 2: Sketch of supercapacitor.

In this note, the charge/discharge behavior of supercapacitors is investigated. Firstly, successive charges/discharges are carried out with a potential scan. In the second part of this note we deal with discharge at constant power.

II – SET-UP DESCRIPTION

Investigations are performed with a VMP3 equipped with a standard board. The characteristics of supercapacitors are described below:

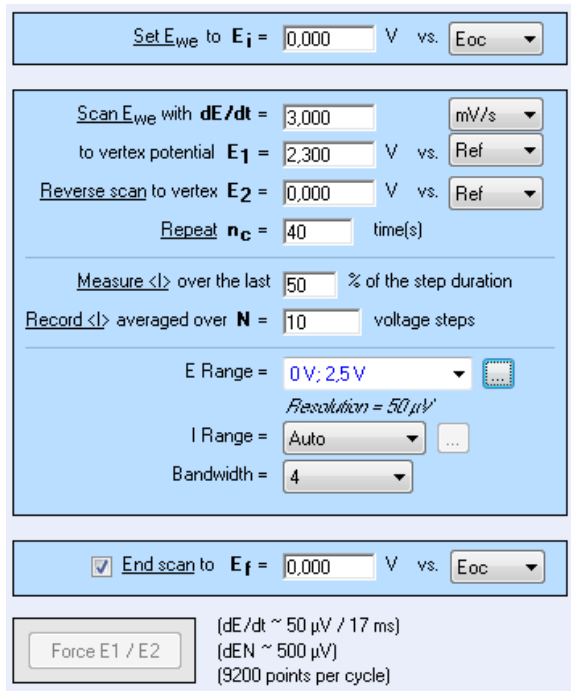
- capacity: 22 F
- maximum operating voltage: 2.3 V
- mass of active material: ~10g

The Supercapacitor is connected to a VMP3 via a standard 2-electrode connection.

III – CHARGE/DISCHARGE CYCLING

As stated above, one of the most important characteristics of an energy storage device is the ability of the device to be charged and discharged many times without any performance loss.

In this paragraph, charge/discharge characterizations are carried out by potentiodynamic sweep at slow scan rate. The cycling of the supercapacitor is performed with 41 cycles of Cyclic Voltammetry (CV). at 3 mV/s between 0 and 2.3 V (Fig. 3).



Set E_{we} to $E_i = 0,000$ V vs. Eoc

Scan E_{we} with $dE/dt = 3,000$ mV/s
to vertex potential $E_1 = 2,300$ V vs. Ref
Reverse scan to vertex $E_2 = 0,000$ V vs. Ref
Repeat $n_c = 40$ time(s)

Measure $\langle I \rangle$ over the last 50 % of the step duration
Record $\langle I \rangle$ averaged over $N = 10$ voltage steps

E Range = 0V; 2.5V
Resolution = 50 μ V
I Range = Auto
Bandwidth = 4

End scan to $E_f = 0,000$ V vs. Eoc

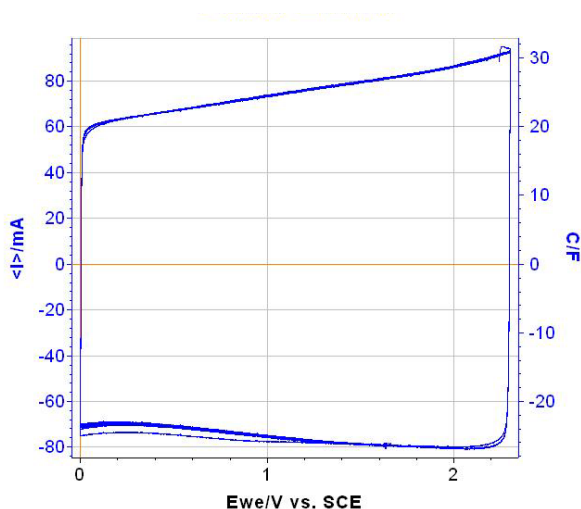
Force E_1 / E_2 (dE/dt ~ 50 μ V / 17 ms)
(dEN ~ 500 μ V)
(9200 points per cycle)

Figure 3: CV settings window.

I vs. E and C vs. E curves are plotted in Fig. 4. These curves show that the current and capacity are stable over 41 cycles. The cycling does not affect the performance of the supercapacitor.

Note: C vs. E curve is plotted thank to the graphic customization ability of EC-Lab®:

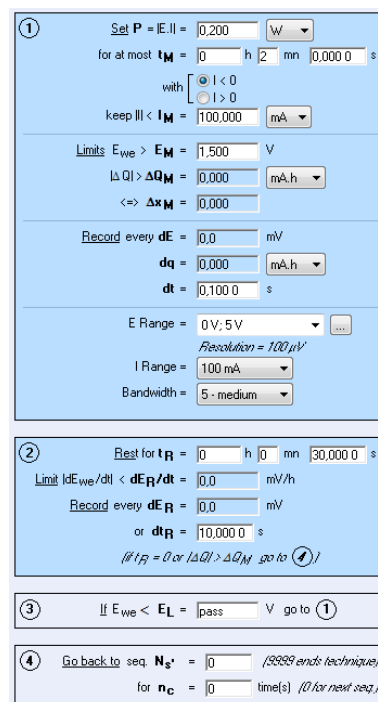
$$C = i \frac{dt}{dE} \quad (1)$$


Figure 4: Charge/discharge cycling.

IV – CONSTANT POWER DISCHARGE

Energy storage devices are commonly represented by a Ragone plot *i.e.* E vs. P . This diagram can be plotted from Constant Power Discharge (CPW) data after mathematical treatment.

The settings of the CPW technique applied to the supercapacitor are described in Fig. 5. The following constant power steps are successively applied to the system: 200, 100, 50, 20, 10, 5 and 1 mW. The plot of Power vs. Energy is shown in Fig. 6.



① Set $P = |E \cdot I| = 0,200$ W
for at most $t_M = 0$ h 2 min 0,000 0 s
with $\begin{cases} I < 0 \\ I > 0 \end{cases}$
keep $|I| < I_M = 100,000$ mA

Limits $E_{we} > E_M = 1,500$ V
 $|dQ| > \Delta Q_M = 0,000$ mA.h
 $\Leftrightarrow \Delta x_M = 0,000$

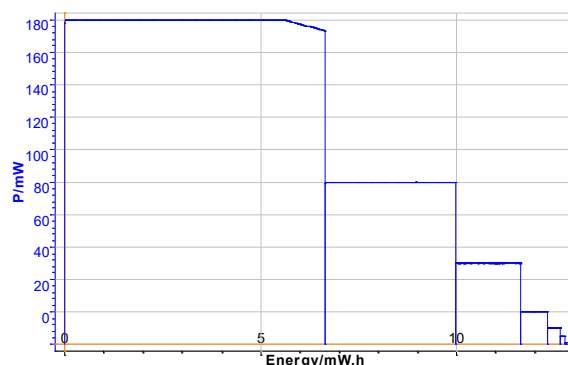
Record every $dE = 0,0$ mV
 $dq = 0,000$ mA.h
 $dt = 0,100 0$ s

E Range = 0V; 5V
Resolution = 100 μ V
I Range = 100 mA
Bandwidth = 5 - medium

② Rest for $t_R = 0$ h 0 min 30,000 0 s
Limit $|dE_{we}/dt| < dE_R/dt = 0,0$ mV/h
Record every $dE_R = 0,0$ mV
or $dt_R = 10,000 0$ s
(*If $t_R = 0$ or $|dQ| > \Delta Q_M$ go to ④*)

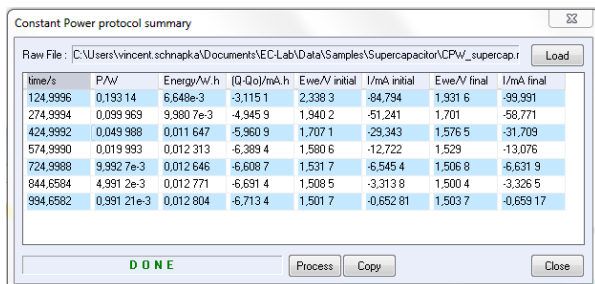
③ If $E_{we} < E_L = \text{pass}$ V go to ①

④ Go back to seq. $N_s^* = 0$ (SSS ends technique)
for $n_c = 0$ time(s) (0 for next seq.)

Figure 5: CPW settings window.

Figure 6: Power vs. Energy plot.

The analysis tool « Constant Power protocol summary » (Fig. 7) allows user to calculate the

energy and potentials and currents at the beginning and at the end of each power step. For this supercapacitor, this energy is around 10 mW/h.



time/s	P/W	Energy/W.h	(Q-Q0)/mAh	Ewe/V initial	I/mA initial	Ewe/V final	I/mA final
124,9996	0,193 14	6,648e-3	-3,115 1	2,338 3	-84,794	1,931 6	-99,991
274,9994	0,099 969	9,980 7e-3	-4,945 9	1,940 2	-51,241	1,701	-98,771
424,9992	0,049 988	0,011 647	-5,960 9	1,707 1	-29,343	1,576 5	-31,709
574,9990	0,019 993	0,012 313	-6,389 4	1,580 6	-12,722	1,529	-13,076
724,9988	9,992 7e-3	0,012 646	-6,608 7	1,531 7	-6,545 4	1,506 8	-6,631 9
844,6584	4,991 2e-3	0,012 771	-6,691 4	1,508 5	-3,313 8	1,500 4	-3,326 5
994,6582	0,991 21e-3	0,012 804	-6,713 4	1,501 7	-0,652 81	1,503 7	-0,659 17

Figure 7: CPW protocol result.

Finally from these calculated values the Ragone diagram can be plotted (Fig. 8).

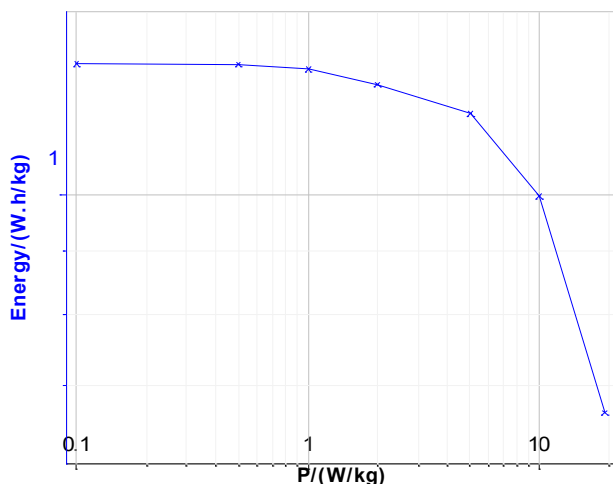


Figure 8: Ragone plot.

V – CONCLUSION

Thank to these potentiodynamic and constant power discharges, it is possible to characterize the cycling performance of the supercapacitor. These characterizations allow users to determine if the supercapacitor being studied fits the need (according to its corresponding pulse output) of the electronic device to be powered.

The determination of the time constant is shown and discussed in the following application note [2].

Data files can be found in :
C:\Users\xxx\Documents\EC-Lab\Data\Samples\Supercapacitor\technique _supercap

REFERENCES

- 1) R. A. Huggins, Solid State Ionics, 13 (2000) 179.
- 2) [Application note #34](#) “Supercapacitors investigations. Part II: time constant determination”

Revised in 08/2019