The Journal of CPRI,
Vol. 13, No. 3, September 2017 pp. 503-512

A study on preliminary screening of 12 V/ 2500 F range lead carbon hybrid ultra-capacitors as energy storage device for solar power applications

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The paper focuses on accepting Hybrid ultra-capacitors as working capacitors from a huge number of unconditioned ones. Hybrid ultra-capacitors of 12 V/2500 F range are evaluated for their performances. Healthy and faulty behavior of these capacitors is analyzed in terms of voltage discharge characteristics. Synthesis of lead carbon hybrid ultra-capacitors of 12 V/2500 F range from electrode to container form is discussed. The steps need to be followed to identify the healthy capacitors from the faulty capacitors are presented. Procedure developed for pre-conditioning of HUCs, performance evaluation and failure analysis results are discussed. From discussion, the condition for acceptance of 12 V/2500 F range Hybrid ultra-capacitor as an energy storage system for solar power applications is formulated.

Keywords: *Pb – C HUC/HUC – lead carbon hybrid ultra-capacitor, constant voltage charging time duration.*

1.0 INTRODUCTION

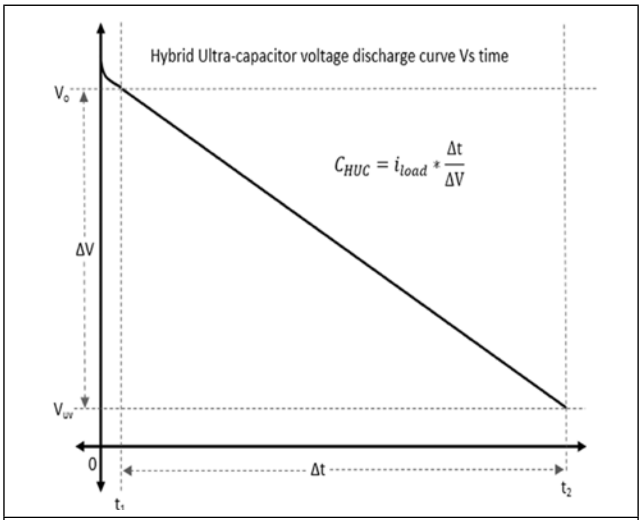

FIG. 1. THE ORETICAL REPRESENTATION OF VOLTAGE DISCHARGE CURVE OF HUC

Conventionally lead acid batteries are the dominant source of energy storage in solar power applications. Due to mass transport phenomenon involved in lead acid batteries, they are suitable for charge/discharge at very low C rates [1]. Faradic charge discharge chemical reactions involved in battery is the reason of mass transport. Considering lead acid battery for solar power applications, battery would fail to charge on cloudy days [2]. Hybrid ultra-capacitors are the challenging next generation energy storage systems capable of having charge storage suitable for solar power applications [3]. HUCs have asymmetric characteristics of energy storage intermediate of battery and Ultra-capacitor. HUC has one terminal of battery electrode and the other terminal of Ultra-capacitor. Charge capability of HUC is not restricted by mass transport as there is an absence of faradic reaction at anode [4]. Capacitance of HUC is dependent on voltage discharge curve of HUC. For a charged HUC, if load current (I_{load}) is applied, voltage drops from V_o at t_1 to V_{uv} at t_2, as shown in Figure 1. Capacitance of HUC is calculated by equation (1), where $\Delta V=V_o-V_{uv}$ and $\Delta t=t_2-t_1$. Mathematically

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$$C_{HUC} = I_{load} * \frac{\Delta t}{\Delta V} = \frac{I_{load}}{slope\ of\ voltage\ discharge\ curve} \quad ...(1)$$

HUCs are capable of charge storage on cloudy days.

2.0 SYNTHESIS OF 12 V/2500 F RANGE HUC MODULE IN CONTAINER

Lead carbon HUCs have one electrode made of lead oxide and the other of activated carbon coated on graphite. Both of the electrodes are immersed in polymeric silica gel with 1.4g/cm^3sulphuric acid electrolyte and separated by a poly-vinyledene fluoride mesh. The internal schematic of single cell and two cell arrangement of 2V HUC cells is shown in Figure 2.

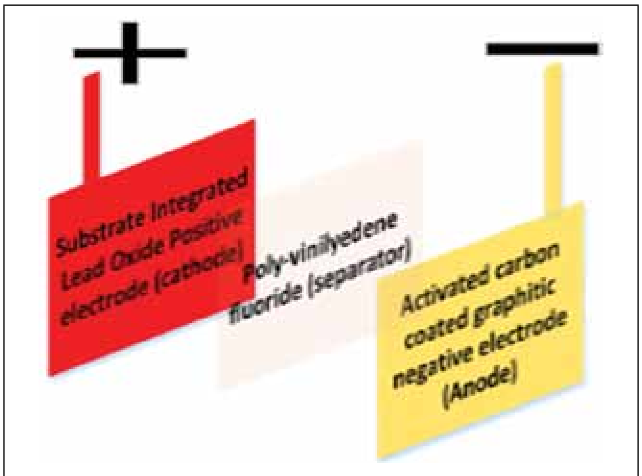

FIG. 2(A). INTERNAL ELECTRO DEREPRESENTATION OF LEAD CARBON HUC CELL FOR HIGH CURRENT

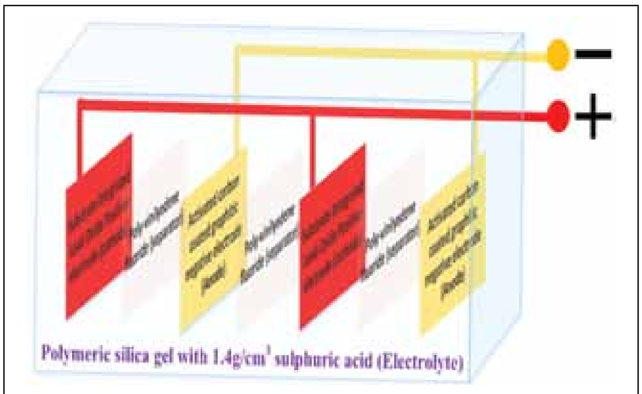

FIG. 2(B). INTERNAL ELECTRODE REPRESENTATION OF LEAD CARBON HYBRID ULTRA CAPACITOR CELL FOR LOW CURRENT

The details of studies made on lead carbon hybrid ultra-capacitors of 12V/kF range are reported somewhere else [5]. Energy storage is in form of pseudocapacitance at lead electrode and electric double layer capacitance at activated carbon electrode. Hence it forms a hybrid asymmetric ultra-capacitor. In brief the making of 12V/2500F range HUC involves synthesis of positive and negative electrodes, electrolyte, group burning and casing.

2.1 Cathode (+ve terminal) Electrode

99.9% pure etched lead sheets are immersed in 6M sulphuric acid. Thin layer of lead sulphate thus formed on the surface of the lead sheet was electrochemically oxidized (by applying potential) to form substrate-integrated lead dioxide positive electrode.

2.2 Anode (-ve terminal) Electrode

85% of activated carbon, 10% of activated charcoal, is mixed with 5% poly (vinylidene fluoride) binder and dimethyl formamide (DMF) solvent to from a carbon ink.The carbon ink is thus applied on iso-statically compressed graphite substrates (current collectors) to form activated carbon coated electrode. These electrodes are dried in an air-oven at $80^{O}C$ for 6 hours before use.

2.3 Electrolyte

Typically, 250ml of silica gel electrolyte was prepared from 5.5% (w/w) fumed silica by mixing 17 g of fumed silica with 100 ml de-ionized water to form aslurry followed by addition of 138ml H_2SO_4 of density 1.4 g/cc and mechanical agitation.

2.4 Group burning

9 positive and 8 negative electrodes are stacked alternatively in a plastic enclosure, with 0.5 mm-thick polyethylene mesh separators followed by group connecting the positive and negative electrodes in parallel. +ve tip coating has tin and

lead combination whereas –ve tip coating is lead. The arrangement is dipped in 6M H_2SO_4 overnight and decant the acid after 24 hours.

2.5 Casing

After filling the casing with electrolyte, positive and negative terminals are brought out for current collecting and energy storage purposes.

3.0 STUDIES TO IDENTIFY HEALTHY HUCs

The lead carbon hybrid Ultracapacitor manufactured by M/s. Mesha energy solution Ltd, Bangalore, are employed for the study. Figure 3 shows a view of the HUCs of rating 12V/2500F. After measuring weight and dimensions as shown in Figure 4, HUCs are checked for any leakage of electrolyte from the container. The Open Circuit Potential (OCP)of HUCs is measured.

FIG. 3. HYBRID ULTRACAPACITOR OF 12V/2500F RANGE EMPLOYED FOR THE STUDY

FIG. 4. VALIDATION OF WEIGHT OF PB – C HUC OF 12V/2500F RANGE

3.1 Acceptance criteria for preliminary screening: The following steps are followed for preliminary screening of HUCs:

i. No leakage of electrolyte

ii. Weight shall be 10 kg with a tolerance of 10 %.

iii. Open circuit voltage shall be 12Vwith a tolerance of 6%, in a charged condition.

HUCs showing OCP as 12V will be considered for further charge discharge procedures. However, HUCs showing OCP less than 12 V will be pre-conditioned so as to improve the OCP to 12 V, as described in Section 3.2.

3.2 Preconditioning of HUCs with OCP less than 12 V

If OCP value of HUC is less than 12V, HUC needs to be pre-conditioned on aregulated power supply. During preconditioning, HUCs are charged in constant current constant voltage (CCCV) mode of 1A, 13.8V for 48h. At the end of 48 h, OCP is measured and the HUCs having less than 12V OCP will be considered as faulty and discarded from further study.

HUCs meeting the preliminary acceptance criteria mentioned at Section 3.1 will be subjected for further test procedure for performance evaluation. The performance of HUCs is evaluated by estimating the capacitance and comparing it with its rated value.

3.3 Test procedure for charge/discharge of HUC

The general procedure used for charging and discharging of betteries has been followed for HUCs also, however, with necessary modifications particularly with reference to C rate. In order to achieve this,the following program is written in MITS-PRO software of ARBIN instruments to identify healthy HUCs. The program with generalized parameters is given as:

Step 1: Rest the HUC for 5 min.

Step 2:Charge the HUC with I_c until it reaches 1.15 times of V_{rating}.

Step 3: Charge the HUC with 1.15 times of V_{rating} for time duration of t_{cv}.

Step 4: Rest the HUC for 5 min.

Step 5: Discharge the HUC with I_{Dis} until it reaches 0.4 times of V_{rating}.

Voltage discharge curve is drawn in origin software, from data obtained in step 5. Voltage discharge curve of an ideal HUC is shown in Figure 1.

3.4 Estimation of capacitance of HUCs

Capacitance of HUC is dependent on voltage discharge curve as shown in Figure 1, and is calculated using eqn (1). The voltage discharge curves of HUCs are analyzed for checking performance of HUCs and also to estimate the capacitance value.

3.5 Acceptance criteria

i. HUC shall charge even with a minimum constant current of 0.5A.

ii. In charge/discharge, HUC shall accept high currents of nearly 5A to 10A, without undergoing thermal runaway and there shall be no electrolyte leakage.

iii. HUCs shall not experience the increase of voltage discharge slope with number of cycles.

iv. OCP shall not fall suddently to lower potentials on loading.

TABLE 1

CAPACITANCE OFFERED BY 12V/2.5KF RANGE HUCS FOR VARIOUS CHARGE DISCHARGE PROFILES

HUC No.	I_c (Amps)	CV (sec)	I_{Dis} (Amps)	Cycle No	Capacitance offered (kF)	Reference figure(s)
HUC 70032	5.0	3600	5.0	02	2.29	5
	5.0	1800	5.0	05	1.84	5
	5.0	3600	5.0	12	1.52	5
HUC 90038	5.0	1800	5.0	06	N.A	6
	5.0	1800	5.0	07	1.07	6
	5.0	1800	5.0	08	0.93	6
	5.0	1800	5.0	09	0.60	6
	5.0	1800	5.0	10	N.A	6
HUC 70046	2.0	3600	2.0	02	1.61	7
	2.0	1800	2.0	04	1.33	7
	2.0	3600	2.0	09	1.75	7
	2.0	7200	2.0	15	2.04	7
	5.0	3600	5.0	01	2.40	8
	5.0	1800	5.0	02	2.20	8
	5.0	3600	5.0	03	2.25	8

v. HUC shall not experience a thermal runaway condition for at least 25 cycles.

vi. There shall be no electrolyte leakage.

TABLE 2

DETAILS OF HUCS SELECTED FOR THE STUDY

HUC IDENTIFICATION NUMBER	OCP (V)	WEIGHT (KG)	CAPACIT-ANCE RANGE (KF)
HUC70032	11.6	9.26	2.5
HUC90038	11.8	9.28	2.5
HUC70046	11.8	9.28	2.5

4.0 RESULTS AND DISCUSSION

Performance of nearly 150 numbers of HUCs has been analyzed. For the sake of brevity, results of three HUCs of same rating are presented and discussed in the paper to compare satisfactory and not-satisfactory performance of HUCs. Details of three HUCs considered for the studies are shown in table I.

4.1 Sequence of charge/discharge procedures

The HUCs were subjected to the following sequence of charge / discharge procedures.

(i) Constant current of 2A at variablet_{cv}.

(ii) Constant current of 5A at constant t_{cv}.

(iii) Constant current of 5A at variablet_{cv}.

T_{cv} was considered from 1800 sec to 3600 sec for the present studies**.**

The performance of three HUCs considered for study is summarized in table II. The capacitance delievered is also summarized in table II.

4.2 Performance analysis of HUC70032

Hybrid ultracapacitor sample HUC70032 has successfully withstood 1st and 2nd charge discharge procedure(refer to Section 4.1). During the 3rd charge discharge procedure, the HUC has shown anerratic behavior, which is analyzed and presented here.

HUC70032 is charged at 5A till 13.8V,and maintained at 13.8V for t_{cv} and discharged at 5A till 4.62V. For first two cyclest$_{cv}$ is maintained at 3600 sec. For cycle 3 to 5, t_{cv} is changed to 1800 sec. For cycle 6 to 12, t_{cv} is maintained again at 3600 sec to check the behavior of HUC for variations in t_{cv} as shown in Table 2.

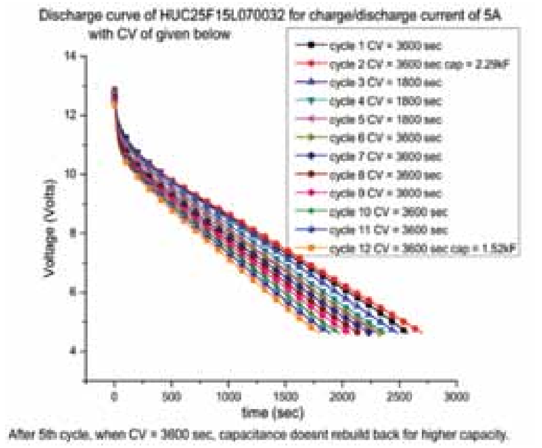

FIG 5. VOLTAGE DISCHARGE CURVES OF HUC70032 FOR 12 CYCLES

It can be seen in Figure 5, that there is an increase in voltage discharge curve slope with number of cycles.

Voltage discharge curves of HUC70032 are shown in Figure 5 for 12 cycles. Capacitance of HUC is estimated from slope of voltage discharge curve. HUC70032 instead of decrease in the slope of voltage discharge curve from cycle 5 to cycle 6, there is an increase in the slope. As can be seen from Table 2, capacitance has dropped down from 2.29 kF to 1.84 kF at the end of 5 cycles, and further dropped to 1.52 kF at the end of 12 cycles.

Increase in the initial voltage drop of voltage discharge curve with number of cycles is also seen in Figure 5. The reason for increase in the internal resistance of HUC is due to electrolyte dehydration. In view of the above behavior the HUC70032 was classified as faulty and discarded.

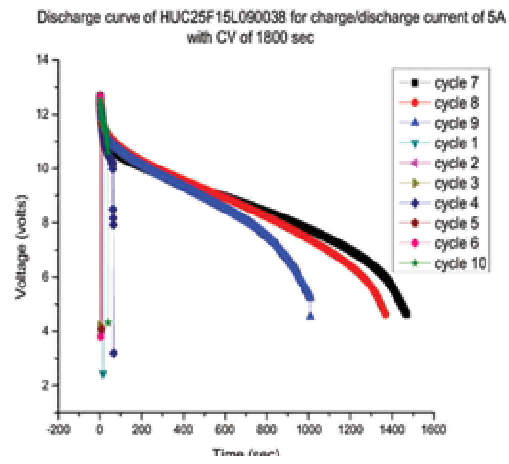

FIG. 6. VOLTAGE DISCHARGE CURVES OF HUC90038 FOR 10 CYCLES.

4.3 Performance Analysis of HUC90038

Hybrid ultra capacitor sample HUC90038 has successfully withstood 1st discharge procedure (refer to Section 4.1). During the 2nd charge discharge procedure, the HUC has shown a peculiar behavior, which is analyzed and presented here.

HUC90038 is charged at 5A till 13.8V, and maintained at 13.8V for t_{cv} and discharged at 5A till 4.62V. t_{cv} is maintained at 1800 sec for 10 cycles. Voltage discharge curves of HUC90038 are shown in Figure 6. As can be seen from Figure 6, this HUC has shown a peculiar behavior. (i) During cycles 1,2,3,4,5 and 6, the curve has shown an infinite slope, indicating sudden fall in discharge curve. (ii) During cycles 7,8 and 9, discharge curve has shown a normal behavior, and estimated capacitance is shown in table II. (iii) During 10th cycle, the discharge curve has again collapsed. Due to inconsistency in capacitance value, the HUC90038 is also classified as faulty and discarded.

4.4 Performance Analysis of HUC70046

Hybrid ultracapacitor sample HUC70046 has shown a statisfactory performance during all the three charge discharge procedures (refer to Section 4.1). Performance of HUC70046 is explained here for all the three procedures.

HUC 70046is charged at 2A till 13.8V, and maintained at 13.8V for t_{cv} and discharged at 2A till 4.62V. For first two cycles t_{cv} is maintained at 3600 sec. For cycle 3 & 4, t_{cv} is changed to 1800 sec. For cycle 5 to 9, t_{cv} is maintained at 3600 sec. For cycle 10 to 15, t_{cv} is maintained at 7200 sec to check the behavior of HUC for variations in t_{cv}.The performance of HUC is summarized as shown in table II. Voltage discharge curves of HUC70046 are shown in Figure 7 for 15 cycles during procedure I. Voltage discharge curves shown in Figure 8 for 03 cycles during procedure II and III.

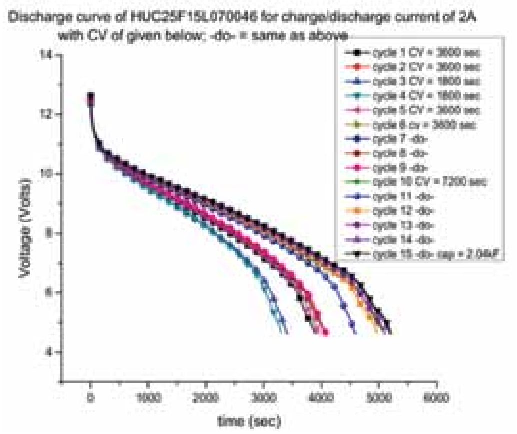

FIG.7. VOLTAGE DISCHARGE CURVES OF HUC70046 FOR 15 CYCLES

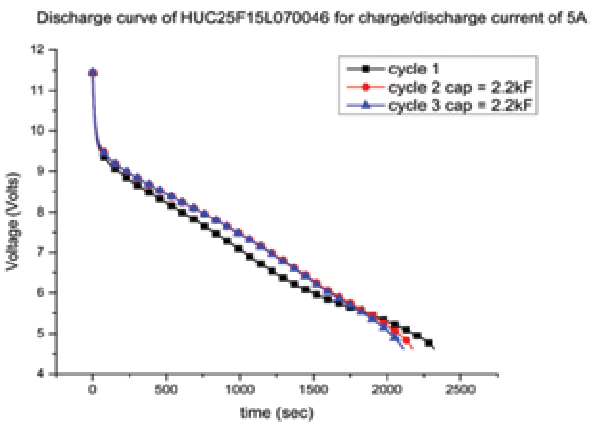

FIG. 8: VOLTAGE DISCHARGE CURVES OF HUC70046 ON 5A FOR VARIOUS T_{CV}

Figure 7 shows the behavior of HUC 70046 on current of 2A with various CV rates whereas Figure 8 shows the behavior of HUC 70046 on higher current rate of 5A for CV rate of 3600, 1800sec and 3600 sec in consecutive cycles.

Sample 70046 is an example of satisfactorily working HUC. It has a better performance of delievering capacitance for various currents and t_{cv}.HUC has delivered a capacitance value of 2.04 kF value, which is close to rated value of 2.5kF after 15 cycles of charge discharge procedure as explained in table II.

The discharge curves in Figure 7 and Figure 8 indicates the progressive decrement in slope of discharge curve, indicating building of capacitance with number of charge / discharge cycles and hence the satisfactory behavior.

5.0 CONCLUSION AND FUTURE WORK

A study has been carried out on a batch of nearly 150 numbers of 12V/2500F range lead carbon hybrid ultra capacitorsto develop a procedure for preliminary screeing of HUCs, which will help in weeding out the faulty HUCs in initial stages itself. A procedure has also been suggested to improve the performance of HUCs through suitable charging technique.

Some of the important experimental findings are:

1. HUCs have been subjected to multiple charge / discharge cycles and the voltage discharge curves are analyzed for checking performance of HUCs and also to estimate the capacitance value.
2. The procedure has has been found to be suitable to identify the faulty capacitors.
3. Applying a constant current charge/ discharge at 2A rate with various$t_{cv,}$ HUCs would deliver better capacitance compared to higher currents.
4. Applying a constant current charge/discharge at 5A rate with various$t_{cv,}$there are cases of HUC failure due to reduction in capacitance.

5. An Optimal test protocol can be obtained for 12V/2500F range capacitor in charging current range of 1A to 3A with various CV rates.
6. This above findings are applicable for 12V/2500F range HUCs. For other rating HUCs, appropriate procedures have to be evolved.

The HUCs which have shown a successful behavior in the present study are further evaluated as energy storage devices for solar power applications.

ACKNOWLEDGEMENT

Author would like to thank ESSI and SSCU labs of IISc Bangalore and officers of Power Capacitors Division of CPRI, Bangalore for valuable guidance and facilities provided.

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