

Research Article

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A photovoltaic stand-alone lighting system with polymeric-silica-gel-electrolyte-based substrate-integrated lead-carbon hybrid ultracapacitors

Abstract: Harnessing solar electricity generated through photovoltaic cells with lead-acid batteries remains the most compelling option at present. But lead-acid batteries have encountered problems in photovoltaic installations, mainly due to their premature failure. To circumvent the aforesaid problem, a new technology referred to as substrate-integrated lead-carbon hybrid ultracapacitor with polymeric-silica-gel electrolyte, is developed in-house and tested for solar-electricity storage for a lighting application. The high-throughput performance tests for the device are conducted at laboratory scale and compatibility of the device for photovoltaic application is evaluated. In doing so, the device is installed with a photovoltaic panel for field test and data are collected from August 2012 through July 2013. The year round field-test data analyzed in the light of the available global-horizontal-irradiance data show attractive performance for the device. It is noteworthy that, unlike lead-acid batteries, seasonal variations in solar radiance exhibit little effect on the performance of the device.

Keywords: Photovoltaic application; Substrate-integrated lead-carbon hybrid ultracapacitor; Polymeric silica gel electrolyte; Cycle-life; Field testing


DOI 10.1515/eetech-2015-0001

Received December 24, 2014; revised April 10, 2015; accepted April 15, 2015

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1 Introduction

Modern society is characterized by a constant need for energy. Nature has provided us with chemical cache of energy as fossil fuels. But the usage of fossil fuels is causing concerns of atmospheric pollution and there is lurking fear that fossil fuels are depleting fast. Nature has also provided us with abundant renewable energy in the form of wind, sun and water. The ancient civilization has always revered the sun and water for the sustenance of life, and the vicissitudes of the last couple of decades have led us to believe that a sustainable energy future must include harnessing the abundant resource of radiant energy from the sun.

The energy of sun light is converted to electrical energy by a photovoltaic cell. During the exposure of the photovoltaic cell to sun light, current is generated which is proportional to the solar insolation. The electricity, generated from photovoltaic panels, can be directly transferred to power grid or can be stored into any storage system, like rechargeable batteries [1–7] or other systems, such as ultracapacitors, super-conducting magnets, compressed air, fly-wheel, etc. [8, 9]. Among these, the lead-acid batteries are the most ubiquitous on account of their cost [10–12]. But lead-acid batteries, for storing solar electricity, have encountered challenges of low state-of-charge depending on the weather conditions owing to sulfation and acid stratification that limit their cycle-life. Consequently, premature replacement of batteries becomes unavoidable [13–15].

In the literature, a comparative study on various formats of lead-acid batteries, namely flooded, gelled, absorbent-glass-mat and hybrid are reported for stand-alone photovoltaic lighting systems [16]. The average state-of-health values for these batteries are found to be 13.3%, 34.7%, 32.8% and 35.9%, respectively, subsequent to the five month solar-lighting service schedule; these performance parameters for the lead-acid batteries are not quite

encouraging for the photovoltaic applications. By contrast, a comparison of capabilities for the various storage technologies suggests hybrid ultracapacitors to be an attractive option [17–21]. Fast charging characteristic is the key metric for successful solar electricity storage with these ultracapacitors. It is found that even on a cloudy day minimal solar insolation is adequate for charging the ultracapacitors nearly fully, which protects the device from its premature failure. The cycle-life of ultracapacitors is a few millions and their operational life is almost equal to the life span of photovoltaic panels. Operating temperature is another vital parameter for the performance of a solar battery. Life times for lead-acid batteries are shortened by higher operating-temperatures [2]. By contrast, ultracapacitors can operate over a wide temperature-range with little degradation in their performance. Accordingly, research and development (R&D) efforts are underway to exploit ultracapacitors for storing solar energy.

We have, for the first time, successfully developed and demonstrated substrate-integrated lead-carbon hybrid ultracapacitors (SI-lead-carbon HUCs) with polymeric-silica-gel electrolyte [22–28]. SI-lead-carbon HUCs are the hybrid of lead-acid battery and electrical double-layer capacitor (EDLC). SI-lead-carbon HUCs have high power-densities and much longer cycle-life than lead-acid batteries as well as higher energy densities than EDLCs. Due to higher power densities, these devices can accept charges quickly. Besides, SI-lead-carbon HUCs can operate over a wide operating temperature range. In the light of the foregoing, SI-lead-carbon HUCs appear to be potential en-

ergy storage systems for photovoltaic applications. Besides, lead-carbon hybrid ultracapacitors are substantially cheaper than any of the presently available ultracapacitors.

In the present study, the high-throughput performance tests for the device are conducted at laboratory scale and compatibility of the device for photovoltaic application is evaluated year round. Interestingly, the year round field-test data analyzed in the light of the available global-horizontal-irradiance data show attractive performance for the device. It is noteworthy that unlike lead-acid batteries, seasonal variation in solar radiance exhibits little effect on the performance of the SI-lead-carbon HUCs making them a compelling option for storing solar energy.

2 Methods

2.1 Assembly of 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitors with polymeric-silica-gel electrolyte

12 V/250 F SI-lead-carbon HUCs were assembled, by connecting six 2 V cells in series, with substrate-integrated lead dioxide positive plates, activated-carbon-based negative plates and silica gel with 1.4 g cm^{-3} aq. sulfuric acid electrolyte employing 0.5 mm thick polyethylene mesh as separator. Weight for a 12 V/250 F SI-lead-carbon HUC was $\sim 2 \text{ kg}$ [27]. In brief, substrate-integrated lead dioxide positive electrodes were obtained by immersing lead sheets in aq. sulfuric acid to form thin layers of lead sulfate on the surfaces of the lead sheets that were electrochemically oxidized to lead dioxide. Five repeated charge/discharge cycles provided the capacity of $\sim 1 \text{ mAh cm}^{-2}$ to substrate-integrated lead dioxide electrodes; the thickness of lead dioxide layer thus formed was found to be $\sim 100 \mu\text{m}$ [26]. Activated carbon coated negative electrodes were fabricated by coating carbon ink obtained by blending 5 wt.% polyvinylidene fluoride (PVDF) binder with adequate amount of dimethylformamide (DMF) solvent, and dispersing 85 wt.% of Meadwestvaco X-090177 activated carbons (USA) and 10 wt.% of activated charcoal (India) onto graphite sheets followed by drying the electrodes in an air-oven at 80°C for 6 h. Optimum loading of the activated carbon on to the graphite sheets was 16 mg cm^{-2} [25–28].

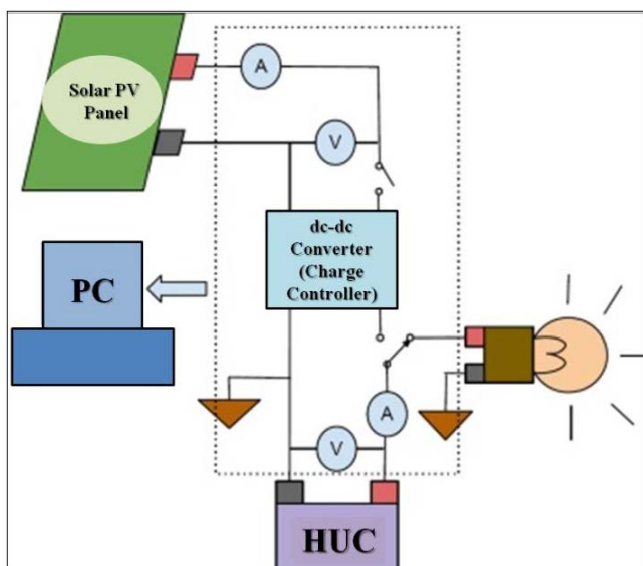


Figure 1: Schematic diagram of photovoltaic stand-alone lighting system with substrate-integrated lead-carbon hybrid ultracapacitor.

2.2 Collection of solar insolation data

A Davis Vantage Pro-2 weather station fitted with silicon photodiode was used for collecting solar insolation data. Solar insolation sensor was connected to a computer and Global Horizontal Irradiance (GHI) data in watts per sq. meter were recorded every minute.

2.3 Collection of device performance test data

Dc performance tests on SI-lead-carbon HUCs device were carried out by BITRODE Instrument fitted with a LCN-Power Module with the device kept into a temperature controlled chamber. Ac impedance studies were performed by Autolab Potentiostat/Galvanostat-Model 30 using Frequency Response Analyser (FRA) software in conjunction with a voltage amplifier.

2.4 Installation of photovoltaic stand-alone lighting system with substrate-integrated lead-carbon hybrid ultracapacitor

A stand-alone photovoltaic lighting system with silica-gel-electrolyte based SI-lead-carbon HUC was installed at Bangalore (India) for field test during August 2012 through July 2013. It is noteworthy that solar insolation is combination of direct beams from the direction of sun and indirect beams scattered by clouds and dust particles that appear from all directions. On a sunny day, the former is predominating while, during a cloudy day, the latter dominates. Accordingly, such studies on energy storage devices under photovoltaic application are strongly installation-site specific [29]. Total stand-alone system comprised a 10W_p photovoltaic panel (Kotak, Model No: KM0010), a 12 V/250 F storage device and a 1 W light emitting diode (LED) lamp. Schematic diagram of stand-alone system is shown in Figure 1. Electrical characteristics for the photovoltaic panel are dictated by open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), maximum voltage (V_{mp}) and maximum current (I_{mp}) under standard test conditions (STC); the respective values being 21.24 V, 0.59 A, 17.64 V and 0.57 A. South-facing panel was installed on the terrace of the building with provision to alter its tilt angle during different seasons of the year according to the illumination angle. It is noteworthy that tilt angle depends on the geographic coordinates of the installation site. For our experiment, we had maintained the tilt angle at 54°, 77° and 100° (an-

gle from vertical direction) during winter, spring/autumn and summer, respectively, to account for the seasonal solar-elevation-angle variations at Bangalore [30]. Photovoltaic panel and storage devices were interfaced to a dc-dc charge-controller. The operating-voltage window for the SI-lead-carbon HUC was maintained between 13.8 V and 6 V through an energy-management system. SI-lead-carbon HUC was charged daily during day and discharged by 1 W LED lamp at the fall of the day during August 2012 through July 2013. The charge and discharge processes were started at about 9 a.m. and 6 p.m., respectively, all through the year.

3 Results and Discussion

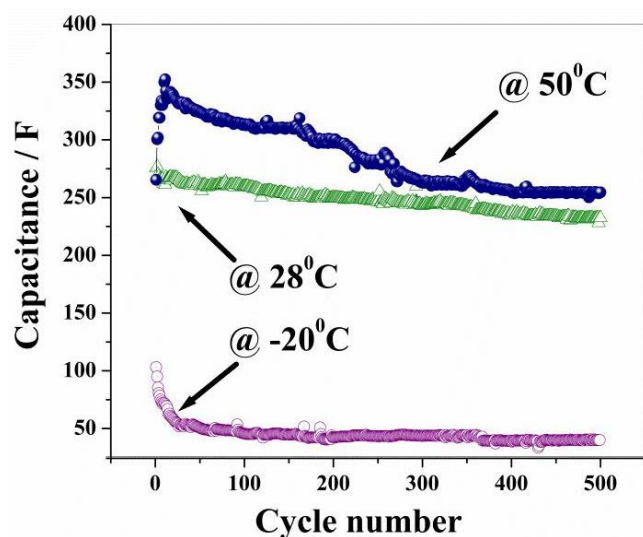
3.1 Compatibility data for 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitor for photovoltaic applications

Performance data for 12 V/250 F gel-based SI-lead-carbon HUC are obtained by constant-current discharge, constant-power discharge, ac impedance spectroscopy, self-discharge voltage loss and float-current experiments at room temperature (28°C) [27]. In field applications, ambient temperature has impact on the performance of any storage device. As a rule of thumb, the operating life of the device will be half of the initial value for every 10°C rise in the operating temperature, which is in accordance with 'Arrhenius law' related temperature dependence of chemical-reaction rate. Capacitance values for 12 V/250 F SI-lead-carbon HUCs are obtained from constant-current discharge data at varying temperatures between -20°C and 50°C [27]. It is observed that due to drastic decrease in electrolyte conductivity owing to freezing at sub-zero temperatures, the capacitance values for the device decrease rapidly. By contrast, at higher temperatures, the capacitance increases due to increase in conductivity. The charge-transfer resistance becomes lower at elevated temperature that helps to overcome the activation of charge-transfer for electrode reactions providing higher performance. The performance data at extreme temperatures are summarized in Table 1 along with room temperature (28°C) data.

Operational life for an energy device is important to support any storage application, especially in photovoltaic systems for specific temperature at installation sites. Premature replacement of storage system increases the cost of power generation. We have tested the device over long-

Table 1: Performance comparison of substrate-integrated lead-carbon hybrid ultracapacitor at various temperatures.

	-20°C	28°C	50°C	
Faradaic Efficiency/%	90	88	87	
@ 0.3 A	102	269	332	
@ 0.6 A	91	255	304	
Capacitance/F	@0.9 A	87	239	280
@1.2 A	82	222	260	
@1.5 A	78	207	242	
Internal resistance/mΩ	215	118	86	
Self-discharge voltage loss for 24 h/%	13	16	17	
Leakage current for 24 h/A	0.016	0.037	0.037	
Parallel resistance for 24 h/Ω	825	377	357	

**Figure 2:** Cycle-life data for 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitor at various temperatures.

lasting charge/discharge cycles in the voltage range between 13.8 V and 6 V at -20°C, 28°C (room temperature) and 50°C. Cycle-life data for 12 V/250 F SI-lead-carbon HUCs are shown in Figure 2, where device is charged and discharged at the load current of 0.3 A. At -20°C, capacitance degradation is fast during initial cycles but subsequently constant capacitance values are recorded. Due to the freezing of electrolyte, the initial drop in performance is observed. After about 25 cycles, consistent performance is observed as the SI lead-carbon HUC gets equilibrated with the surrounding temperature. Accordingly, appropriate sizing of the devices is desirable to meet the energy demand. At 50°C, capacitance values decrease with concomitant increase in internal resistance due to drying of the electrolyte. At elevated temperatures, the rate of parasitic reactions and positive plate corrosion increase lead-

ing to performance degradation of SI lead-carbon HUC. At 28°C, cyclic performance is observed to be good. Long cycle-life has been achieved for SI-lead-carbon HUCs due to the use of EDLC electrode as negative plates and thin layer of lead dioxide electrode as positive plates, which are prudent for photovoltaic applications.

The requirements for a solar energy storage system are high cycle-life, high energy density, fast charging, low self-discharge, wide operational-temperature, mechanical robustness, low maintenance and low cost [4]. 12 V/250 F silica gel electrolyte based SI-lead-carbon HUC has all the above characteristics, and hence, would be an attractive candidate for solar electricity storage.

3.2 Field-test data for 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitor in photovoltaic applications

Data logging unit for photovoltaic panel-SI-lead-carbon HUC assembly collects the concomitant voltage and input/output current data every second during charge/discharge of the device. Time integral of current gives the data for total charge input and output during its charge and discharge, respectively. Multiplication of device voltage and instant current as input or output provides power data. Total energy input and output for the device during charge and discharge, respectively, can also be calculated from time integral of power data. Total charge input at the end of the charge and output at the end of discharge are depicted in Figure 3(a). Similarly, total energy input at the end of charge and output at the end of discharge are recorded daily in Figure 3(b). The data profile in Figure 3(b) is similar to Figure 3(a). Figure 3(c) shows

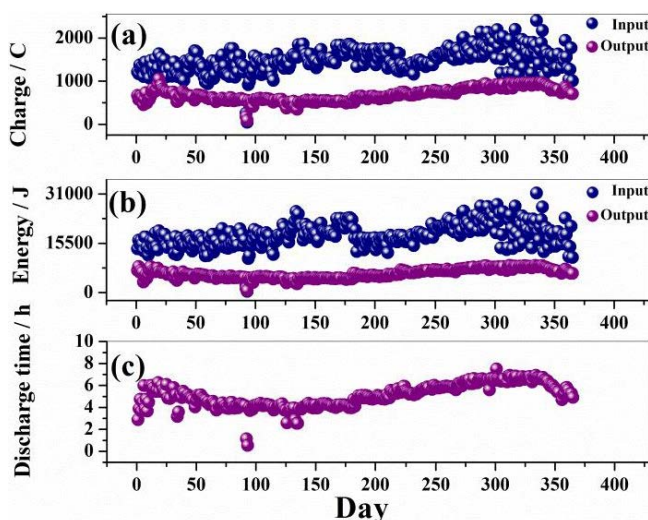


Figure 3: One year field testing data of 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitor for photovoltaic application (a) Charge input and output per day, (b) Energy input and output per day, (c) per day discharge time of device under 1 W LED load.

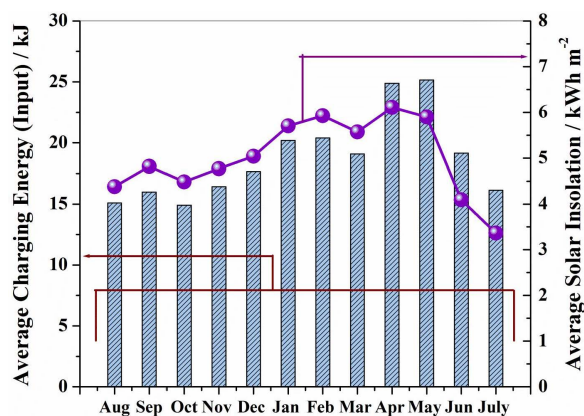


Figure 4: Distribution data for average charging energy of 12 V/250F substrate-integrated lead-carbon hybrid ultracapacitor with respect to solar insolation.

discharge time for the device for voltage range between 13.8 V and 6 V under 1 W LED load. The charge input profiles in Figure 3(a) and 3(b) are noisier due to variation in sunshine on different days of the year. By contrast, discharge output profiles are quite smooth throughout the year exhibiting the performance consistency of storage device. On normal monsoon days, especially during the month of June, July, August and September, the device is charged fully and provides desired output during night at 1 W LED load. As seen in Figure 3, we do not observe any drastic degradation in performance of the SI lead-carbon HUC during monsoon. On October 31, 2012 and November 1, 2012 the device was not completely charged

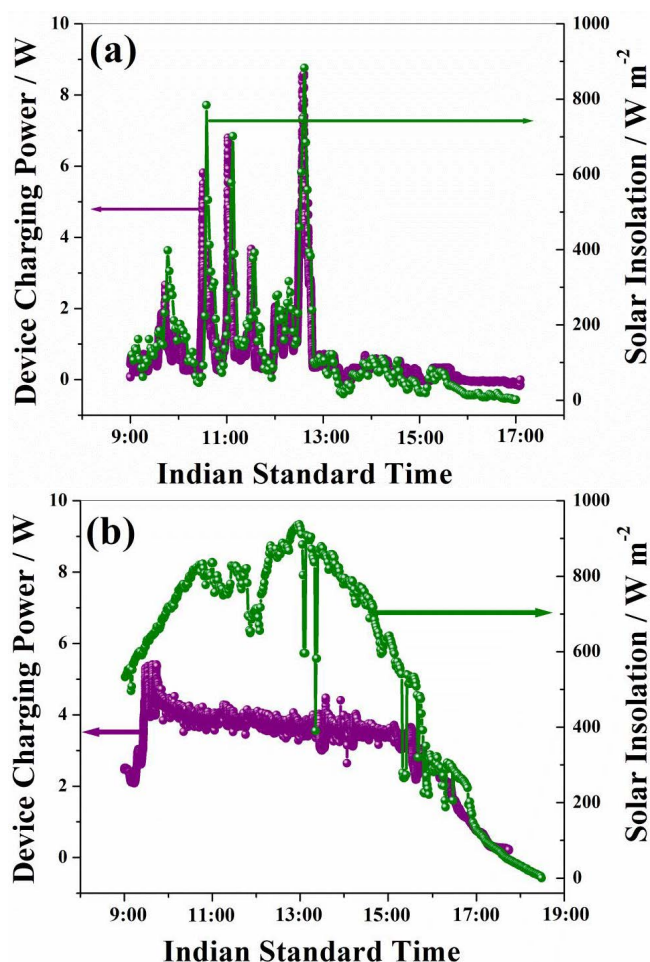


Figure 5: Concordance of charging power with solar insolation as a function of charging time (a) data for 4th December, 2012 (cloudy) and (b) data for 5th May, 2013 (sunny).

due to depleted solar insolation. The respective solar energy values on October 31, 2012 and November 1, 2012 are 642.5 and 541.5 Wh m^{-2} compared to the monthly average of 4483 Wh m^{-2} for October 2012 and 5209 Wh m^{-2} for November 2012. But expect these two days, there has been no difficulty in charging the device even during monsoon also. It is noteworthy that solar insolation on a moderately cloudy day is adequate for charging the SI lead-carbon HUC due its fast charging feature [26, 27].

Monthly average for charging energy input data are calculated and presented in Figure 4. The trend for average charging energy during each month matches well with the average solar insolation (kWh m^{-2}) data for the respective month. Considering two arbitrary days, namely a cloudy day on December 4, 2012 and a sunny day on May 5, 2013, the charging power has been plotted as a function of charging time along with the solar insolation (W m^{-2}) during that period and data are presented in Figure 5(a) and 5(b),

respectively. It is evident from Figure 5(a) that the charging characteristics for SI-lead-carbon HUC depend on solar insolation and follow the solar insolation profiles, when the solar insolation is limited. In case of the sunny day, device charging phenomenon is complete and saturated as indicated in Figure 5(b). The end portion of the charging profile in Figure 5(b) after about 4 p.m. declines due to limited solar insolation, where solar insolation and charging profile are well matched.

The monthly average for discharging energy output data are computed and shown in Figure 6. It is noteworthy that the monthly average discharge energy data do not follow the solar insolation profile unlike the charging characteristics. It is also observed that the discharge energy distribution corresponds to the average sunshine hours for the month. During winter season, the sunset time is earlier than in summer. As the discharging process for the device is started at 6 p.m. throughout the year, the leakage of energy from the device before starting the discharge process happens to be more in winter than in summer. Accordingly, the discharge energy distribution trend matches with average sunshine hours during the month. The self-discharge energy loss due to leakage behavior of the device is nearly 20% for first one hour after the end of the charging process [27]. As the discharge energy variation does not depend on the solar insolation directly, it is clear that the charging process is almost complete in all seasons with moderate solar insolation, which is a key feature for SI-lead-carbon HUC. Higher input energy during charging for longer hours throughout summer days prevents the leakage of energy from the device, which manifests as higher output discharge energy. The availability

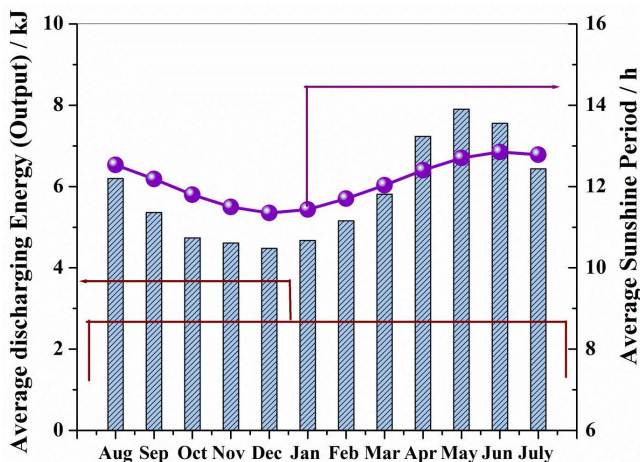


Figure 6: Distribution data for average discharging energy of 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitor with respect to sunshine hour.

of required charging energy for SI-lead-carbon HUC is almost similar throughout the year with moderate solar insolation, irrespective of seasonal variations.

Discharge time data for the device using 1 W LED lamp load are analyzed monthly in Figure 7, where maximum, minimum and average data per month are plotted. It is seen that the average value always is close to the maximum value, which is indicative of good performance for the device. From August to December, the maximum and minimum values are quite different while, from January to July, there is some difference in these values, suggesting better performance for the device during sunny days. In summer, the number of sunshine hours is more than in winter. Hence, during August to December, the average discharge time is lower than during January to May. The average discharge time for the month of June and July is lower than in May, due to the onset of monsoon. During December, the average discharge time is lowest while, during May, it is highest. Hence, it can be surmised that the stand-alone photovoltaic application with SI-lead-carbon HUC does not encounter any difficulties during rainy season. At the end of one year, little capacitance degradation under 1 W LED load discharge due to repetitive cycling is observed. The analysis of data implies that the field testing of 12 V/250 F silica gel electrolyte based SI-lead-carbon HUC under a stand-alone photovoltaic application is successful.

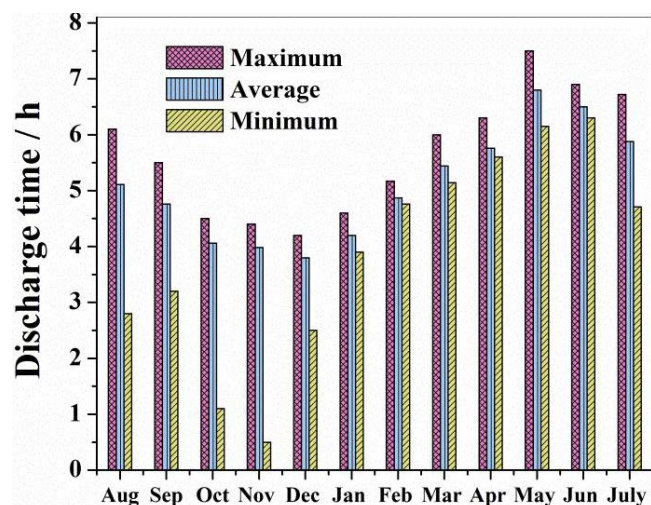


Figure 7: Monthly analysis for discharge time of substrate-integrated lead-carbon hybrid ultracapacitor under 1 W LED load.

3.3 Performance testing data for 12 V/250 F substrate-integrated lead-carbon hybrid ultracapacitor after one year of field testing

Laboratory experiments are performed on the device after one year of field test under similar protocol as followed during the performance testing before starting the field test. It is seen that there is little change in performance. The capacitance values are observed to be 260, 246, 229, 214 and 201 F at 0.3, 0.6, 0.9, 1.2 and 1.5 A current loads, respectively. The faradaic efficiency and internal resistance recorded after one year of field test are 90% and 0.120Ω , respectively. The self-discharge voltage loss, leakage current and parallel resistance data for 24 h data are 18%, 0.038 A and 347Ω , respectively. All these data are comparable with the data presented in Table 1 at room temperature (28°C). Accordingly, SI-lead-carbon HUC shows almost no performance degradation at the end of one year of rigorous field tests affirming that the device has excellent potential for photovoltaic applications in grid power deficient remote areas.

4 Conclusions

A 12 V/250 F silica gel electrolyte based substrate-integrated lead-carbon hybrid ultracapacitor is installed with a photovoltaic panel for solar electricity storage. One year field test data suggests that the device has potential for such an application due to its unique features. The device has the characteristics of both the battery and electrical double-layer capacitor that help it exhibit high energy density and long cycle-life. These two characteristics are imperative for solar electricity-storage-application. Low maintenance and mechanical robustness of the device also help to keep the device at installation site without any major protection. The device can be installed for stand-alone lighting systems powered by photovoltaic panel over a wide range of operating temperatures.

Acknowledgement: Financial support from Department of Science & Technology, Government of India, New Delhi and Indian Institute of Science, Bangalore under its Energy Storage Systems Initiative is gratefully acknowledged. AB thanks Council of Scientific and Industrial Research (CSIR), New Delhi for a Senior Research Fellowship.

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