Studies on 12 V substrate-integrated lead-carbon hybrid ultracapacitors

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Abstract. A cost-effective 12 V substrate-integrated lead-carbon hybrid ultracapacitor is developed and performance tested. These hybrid ultracapacitors employ flexible-graphite sheets as negative plate current-collectors that are coated amperometrically with a thin layer of conducting polymer, namely poly-aniline to provide good adhesivity to activated-carbon layer. The positive plate of the hybrid ultracapacitors comprise conventional lead-sheet that is converted electrochemically into a substrate-integrated lead-dioxide electrode. 12 V substrate-integrated lead-carbon hybrid ultracapacitors both in absorbent-glass-mat and polymeric silica-gel electrolyte configurations are fabricated and characterized. It is possible to realize 12 V configurations with capacitance values of ~ 200 F and ~ 300 F, energy densities of ~ 1.9 Wh kg^{-1} and ~ 2.5 Wh kg^{-1} and power densities of ~ 2 kW kg^{-1} and ~ 0.8 kW kg^{-1} , respectively, having faradaic-efficiency values of ~ 90 % with cycle-life in excess of 100,000 cycles. The effective cost of the mentioned hybrid ultracapacitors is estimated to be about ~ 4 US\$/Wh as compared to ~ 20 US\$/Wh for commercially available ultracapacitors.

Keywords. Hybrid-ultracapacitor; flexible-graphite; poly-aniline; cost-effective ultracapacitor.

1. Introduction

The use of storage batteries is mandatory to further the reliability, stability and security of electrical power in futuristic grids as also to store energy from intermittent renewable sources of energy, namely solar and wind, owing to their small footprint and flexible sitting.¹ Ironically, however, lead-acid batteries are unable to meet the long-life and quick-charge requirements for the aforesaid applications, and the advanced batteries, which have become available in recent years, are expensive. Since the negative plate happens to be a limiting factor in the life span of the lead-acid batteries,² efforts have been expended in the literature to mitigate the problem.³ The most logical approach to counter the aforesaid problem has been to look for alternatives to the conventional lead negative-plates or to reduce their contribution to battery. Ultracapacitor electrodes have been chosen for this purpose. For example, Axion Power International has replaced the negative-plates of valve regulated lead-acid batteries with ultracapacitor plates.⁴ CSIRO and Furukawa Battery have developed and tested a battery called the Ultra-battery with negative plates comprising half-regular-lead plate and half-ultracapacitor plate.^{2,5} Firefly Energy used carbon foam instead of a lead grid to hold the negative active-material and to maintain a stable three-dimensional

structure of negative active-material with widely open pores.⁶ But as the Axion design uses a metallic substrate for its ultracapacitor plates, these could be prone to corrosion albeit being protected with a corrosion-resistant coating. Also, the positive plate in the device is still pasted-type that limits its rate capabilities and degree of positive active-material utilization.²

Earlier,^{7–18} we have reported a 12 V substrate-integrated lead-carbon hybrid ultracapacitor with positive plates as substrate-integrated lead dioxide plates and negative plates as activated-carbon-coated isostatically-compressed-graphite sheets that are cost-intensive. In this study, we report a simple and cost-effective approach to develop substrate-integrated lead-carbon hybrid ultracapacitors by employing poly-aniline coated flexible-graphite sheets in place of isostatically-compressed-graphite plates.

We have developed and performance tested 12 V substrate-integrated lead-carbon hybrid ultracapacitors with carbon-pasted poly-aniline-coated cost-effective flexible-graphite sheets obtained by compression of exfoliated graphite as negative plates and substrate-integrated lead dioxide sheets as positive plates.¹⁹ 12 V substrate-integrated lead-carbon hybrid ultracapacitors are assembled with aforesaid negative and positive plates in two variants, namely absorbent-glass-mat and polymeric-silica-gel configurations that yield capacitance values of ~ 200 F and ~ 300 F, respectively, with charge-discharge cycle-life in excess of 100,000

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cycles at a faradaic efficiency of $\sim 90\%$.¹⁹ As substrate-integrated lead-carbon hybrid ultracapacitors promise to meet the long-life and quick-charge requirements, they are likely to find place into a wide array of storage applications. Besides performance characteristics and safety issues, another important factor is the cost of the ultracapacitors. At present, the cost of the commercially available ultracapacitors is typically ~ 20 US\$/Wh.²⁰ By contrast, based on the bill of materials, the substrate-integrated lead-carbon hybrid ultracapacitors reported here are expected to cost ~ 4 US\$/Wh.

2. Experimental

2.1 Poly-aniline coating on to flexible-exfoliated-graphite sheets

0.3 mm thick flexible-graphite sheets (density: 1.1 g cm^{-3} and tensile strength: 6.25 MPa) from Changyi Dongfeng Sealing Materials (China) were used as negative current-collectors. The sheets were amperometrically coated with a thin layer of poly-aniline in a 3-electrode cell assembly using 0.5 M sulfuric acid (Sigma Aldrich) and 0.2 M aniline (Sigma Aldrich) solution under nitrogen-purging. Flexible-graphite sheets were coated with poly-aniline potentiostatically at 0.75 V vs. Ag/AgCl electrode (0.197 V vs. SHE),²¹ and were subsequently washed copiously with distilled water followed by drying at room temperature ($\sim 28^\circ\text{C}$).

Poly-aniline film was electrochemically characterized by cyclic voltammetry. Poly-aniline film was physically characterized by Fourier-Transform-Infrared (FT-IR) spectrum, powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). Cyclic voltammograms for poly-aniline film was recorded on an Autolab Potentiostat/Galvanostat-Model 30. FT-IR spectrum for poly-aniline film was recorded on a Spectrum 1000-Perkin Elmer FT-IR Spectrophotometer. PXRD pattern for the film were recorded on a Philips X'pert-Pro X-ray Diffractometer equipped with X'cellerator detector, at scan speed ($^\circ/\text{s}$), step size ($^\circ$) and time per-step (s) of 0.053, 0.016 and 0.30, respectively, using a CuK_α radiation source. SEM images were obtained using ZEISS ULTRA 55 and FEI ESEM-Quanta 200 instruments for cross-sectional and surface morphologies, respectively.

2.2 Preparation of negative electrodes

Carbon ink was prepared by blending 5 wt.% polyvinylidene fluoride (PVDF) binder with adequate

amount of dimethylformamide (DMF) solvent in conjunction with 85 wt.% of Meadwestvaco carbon X-090177 form Meadwestvaco (US) and 10 wt.% of activated charcoal from S. D. Fine Chem (India) into it. Flexible-graphite sheets ($4.5 \text{ cm} \times 7 \text{ cm}$) with tin-lead alloy plated tags ($1 \text{ cm} \times 1.5 \text{ cm}$) were coated with $\sim 300 \mu\text{m}$ thick layer of carbon ink on either side as described elsewhere.^{7,8}

2.3 Preparation of positive electrodes

Substrate-integrated lead-dioxide electrodes were used as positive plates that were prepared from 99.9 % pure lead sheets by dipping them overnight in 6 M aqueous (aq.) sulfuric acid, and subsequently subjecting them to five consecutive electrochemical charge-discharge formation cycles with a dc current-density of 1 mA cm^{-2} . Since the lead sheet as substrate and electrochemically formed lead-dioxide are integral part of the same electrode, the electrodes are termed as substrate-integrated lead dioxide electrodes. The specific capacity of the substrate-integrated lead-dioxide electrodes were $\sim 1 \text{ mAh cm}^{-2}$ as shown in figure 1. The electrodes were characterized by powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).⁷

2.4 Assembly of 12 V substrate-integrated lead-carbon hybrid ultracapacitors

12 V substrate-integrated lead-carbon hybrid ultracapacitors with co-located terminals were assembled with

Figure 1. Discharge data for substrate-integrated lead dioxide electrodes vs. Mercury/Mercurous Sulfate (MMS) reference electrode during formation cycles. Inset: Capacity increment for lead dioxide electrode with cycle number.

six 2 V cells connected in series. Each 2 V cell was assembled using nine substrate-integrated lead dioxide positive electrodes and eight carbon-coated flexible-graphite negative electrodes with separators and sulfuric acid electrolyte as shown in figure 2a. The schematic representation of 12 V device is shown in figure 2b. At present, starved electrolyte is used in place of free-flow electrolyte in maintenance-free lead-acid batteries with the liquid electrolyte entrapped into a porous matrix or immobilized into a three-dimensional gel network. Absorbent-glass-mat (AGM) is a silica-based porous material that acts as separator and concomitantly soaks the electrolyte. Device with such a configuration is

called hybrid ultracapacitor with AGM-configuration. Alternatively, the electrolyte can be immobilized in a three-dimensional silica-gel network system where sulfuric acid participates in the three-dimensional H-bonding framework; this configuration is known as gel-configuration. The weights for 12 V devices with AGM and gel-configurations were ~ 1.5 kg.

2.5 Characterization of hybrid ultracapacitors

12 V substrate-integrated lead-carbon hybrid ultracapacitors with AGM and gel configurations were

Figure 2. Schematic representations for (a) 2 V substrate-integrated lead-carbon hybrid ultracapacitor cell and (b) 12 V substrate-integrated lead-carbon hybrid ultracapacitor realization.

Figure 3. Cyclic voltammogram for poly-aniline-coated flexible graphite current-collector in 6 M sulfuric acid in three-electrode system against Mercury/Mercurous Sulfate (MMS) reference electrode.

characterized by electrochemical performance test using regular ultracapacitor-test protocol, namely measurements on faradaic efficiency, internal resistance, response time, capacitance, energy density, power density, self-discharge, leakage current, parallel resistance and cycle life.

All performance tests on the ultracapacitors were carried out using Autolab Potentiostat/Galvanostat-Model

30 and Bitrode instrument fitted with a LCN-Power Module. Electrochemical impedance spectroscopic studies were performed with an Autolab Potentiostat/Galvanostat-Model 30 using Frequency Response Analyser (FRA) software in conjunction with a voltage amplifier. All the experiments were performed at room temperature ($\sim 28^\circ\text{C}$).

3. Results and Discussion

3.1 Electrochemical and physical characterization of poly-aniline film

Poly-aniline film is electrochemically characterized by cyclic voltammetry in a 3-electrode cell assembly. Poly-aniline-coated flexible-graphite sheet and dimensionally-stabilized-graphite plate are used as working and counter electrodes, respectively. A scan rate of 10 mV s^{-1} is applied to working electrode against Mercury/Mercurous sulfate (MMS) reference electrode (0.573 V vs. SHE); and the cyclic voltammogram thus obtained is shown in figure 3. Poly-aniline exhibits four characteristic peaks that are governed by two oxidation and two reduction processes according to scheme 1. There are various forms of poly-aniline with varying imine and amine segments.²¹ Three redox states of poly-aniline range from the fully-reduced leucoemeraldine (LE) through partially-oxidized

Scheme 1. Redox states of poly-aniline: fully-reduced leucoemeraldine (LE), partially-oxidized emeraldine (EM) and fully-oxidized pernigraniline (PE).

Figure 4. FT-IR spectrum for poly-aniline film.

emeraldine (EM) to the fully-oxidized pernigraniline (PE) state. In the cyclic voltammogram, Peak I refers to LE $\rightarrow$ EM, Peak II refers to EM $\rightarrow$ PE, Peak III refers to PE $\rightarrow$ EM, and Peak IV refers to EM $\rightarrow$ LE. The general structure of poly-aniline is $[(\text{-B-NH-B-NH-})_y(\text{-B-N=Q=N-})_{1-y}]_n$, where B and Q represent the C_6H_4 ring in the benzenoid and quinonoid forms, respectively.

Figure 4 shows the Fourier-Transform-Infra-Red (FT-IR) spectrum for electrodeposited poly-aniline on to the flexible graphite electrodes.^{22,23} Transmittance peaks at 3470 cm^{-1} and 2932 cm^{-1} refer to N-H stretching mode and C-N stretching of secondary aromatic amine (-N-benzenoid-N-), respectively. Peaks at 1650 cm^{-1} and 1473 cm^{-1} represent C=N and C=C stretching mode for quinoid and benzenoid rings, respectively. The band at 1303 cm^{-1} refers to C-N stretching (-N-benzenoid-N-) vibration, and the band at 1233 cm^{-1} is due to stretching of the C-N^+ polaron structure formed on acid doping of the emeraldine (EM) base of poly-aniline, which is characteristic of electrically conducting form of doped poly-aniline.²⁴ C=N stretching (-N=quinoid=N-) vibration mode appears at 1107 cm^{-1} in FT-IR spectrum, and the band at 801 cm^{-1} represents out of the plane aromatic C-H bending in 1, 4-disubstituted aromatic ring.

PXRD pattern for poly-aniline film is shown in figure 5. Crystalline nature of coated poly-aniline film is seen from the sharp peaks in PXRD pattern. In figure 5, an intense peak appears at $2\theta \sim 26.88^\circ$ with $3.31\text{ \AA}$ d-spacing due to (200) planes.²⁵ The peak at $2\theta \sim 54.95^\circ$ with $1.66\text{ \AA}$ d-spacing is attributed to (400) planes.

Electrodeposited poly-aniline film has also been characterized by SEM images. Thickness of the film

Figure 5. PXRD pattern for poly-aniline film.

as estimated from cross-sectional SEM image is about $20\text{--}25\text{ }\mu\text{m}$ as shown in figure 6a. Comparative surface morphologies for pristine and poly-aniline coated flexible graphite sheet are shown in figure 6b and c. It is seen that poly-aniline coated surface exhibits large micro-roughness compared to the smoother pristine-graphite-surface. From figure 6c, it is found that $\sim 0.3\text{ }\mu\text{m}$ poly-aniline particles are present on to the surface of flexible-graphite, which make the surface rough and provide high adhesivity to carbon coating. We have also carried out a tape-peel-off test and have observed that the carbon layer poorly adheres to pristine flexible graphite surface whereas it has high adhesivity with poly-aniline-coated surface. Accordingly, it is inferred that poly-aniline film helps reducing the interfacial contact-resistance between the flexible-graphite sheet and the carbon-layer.

3.2 Effect of poly-aniline on electrochemical performance of ultracapacitors

Effect of poly-aniline coating on to the flexible-graphite current-collectors is studied with 1.2 V Electrical Double-Layer Capacitor (EDLC), and relevant data are presented in figure 7. Cyclic voltammograms for 1.2 V EDLC, both with pristine and poly-aniline coated flexible-graphite current-collectors, are shown in figure 7 a. EDLCs with poly-aniline coated current-collector exhibit more rectangular cyclic voltammograms in relation to the one with pristine sheet.²⁶ EDLCs with pristine current-collector also exhibit more resistive behaviour. Interestingly, the capacitance values for pristine and poly-aniline-coated EDLCs happen to be nearly similar, namely 130 F and 138 F , respectively.

Figure 6. (a) Cross-sectional SEM image for poly-aniline coating, (b) surface morphology of pristine flexible graphite sheet and (c) surface morphology of poly-aniline coated flexible graphite sheet.

Figure 7. (a) Cyclic voltammograms at 10 mV s^{-1} scan rate and (b) Nyquist plots in 5 mHz to 100 kHz frequency range for 1.2 V EDLC cells with pristine and poly-aniline (PANI) coated flexible graphite current-collectors.

Internal-resistance data are obtained from the high-frequency X-intercept in Nyquist plots of electrochemical impedance spectroscopy,²⁶ and are presented in figure 7b. EDLCs with poly-aniline coated current-collector exhibit lower internal-resistance as compared to those with pristine current-collector, the respective values being $105 \text{ m}\Omega$ and $170 \text{ m}\Omega$. There are mainly two reasons attributed to reduction in the internal resistance of poly-aniline coated flexible-graphite current-collectors: (a) the layer of conducting material in between active-material and current-collectors facilitates flow of electrical charges from electrodes surface to cell terminals through current-collectors and (b) provides proper contact between active-material and current-collectors due to good adhesivity.

3.3 Performance tests on 12 V substrate-integrated lead-carbon hybrid ultracapacitors

12 V substrate-integrated lead-carbon hybrid ultracapacitors in AGM and gel-configurations are performance tested, and data are described below. Faradaic

Figure 8. Voltage vs. time data at constant-current (0.3 A) charge/discharge in the operating window between 6 V and 13.8 V for 12 V substrate-integrated lead-carbon hybrid ultracapacitors.

efficiencies are calculated for 12 V substrate-integrated lead-carbon hybrid ultracapacitors from the ratio of charge output and input using constant-current (0.3 A) charge-discharge profiles as shown in figure 8, and the data are presented in table 1. It is found that both AGM and gel hybrid ultracapacitors exhibit almost similar faradaic efficiencies. The voltage window is chosen between 6 V and 13.8 V to avoid overcharging of the devices. It is noteworthy that the aqueous electrolyte can dissociate at higher voltages that increases the internal resistance and limits the cycle-life of the device.

Internal-resistance and response-time values for 12 V hybrid ultracapacitors are estimated from the electrochemical impedance data at 12 V from Nyquist and Bode plots shown in figure 9 and figure 10a and b, respectively. The internal-resistance value is higher for gel-based hybrid ultracapacitors in relation to AGM-based hybrid ultracapacitors, primarily due to restricted

Figure 9. Nyquist plots for 12 V substrate-integrated lead-carbon hybrid ultracapacitors with AGM and gel configurations at 12 V.

ionic movement through three-dimensional silica-gel network. By contrast, AGM separators can be compressed that helps bringing positive and negative plates

Figure 10. Response time calculations for 12 V substrate-integrated lead-carbon hybrid ultracapacitors with (a) AGM and (b) gel configurations at 12 V.

Table 1. Performance data for 12 V substrate-integrated lead-carbon hybrid ultracapacitors in AGM and gel configurations.

	Unit	AGM	Gel
Rated Capacitance	F	200	300
Faradaic Efficiency	%	94	92
Internal Resistance	mΩ	148	182
Response Time	s	3.3	11.5
Leakage Current over 24 h	mA	17	33
Parallel Resistance over 24 h	Ω	776	400
Self-Discharge rate over 24 h	%	14	16
Energy Density	Wh/kg	1.90	2.54
Power Density	W/kg	2075	795

in close contact, reducing internal-resistance of the hybrid ultracapacitors. Response time for substrate-integrated lead-carbon hybrid ultracapacitors needs to be measured for realising their fast charge-discharge capabilities, and can be estimated from Bode plot (phase vs. frequency) using ac impedance spectroscopy. In the Bode plot, the resistance and capacitive reactance are equal at phase angle of -45° ; the corresponding frequency being called as breaking frequency.²⁶ Beyond this frequency, capacitive reactance becomes larger than resistance, and the time corresponding to the breaking frequency is represented as response time of the capacitor. The internal-resistance and response-time data are presented in table 1. Response-time data for AGM-based hybrid ultracapacitors is much lower than the gel-based hybrid ultracapacitors; lower response-time value for AGM-based hybrid ultracapacitors is indicative of their higher power in relation to gel-based hybrid ultracapacitors.

Capacitance data are analyzed from the discharge profiles at constant-currents between 0.3 A and 1.5 A for both AGM and gel-based hybrid ultracapacitors, and respective discharge data are shown in figure 11a and b. Capacitance values are estimated from the ratio of the discharge-current and the slope of discharge profiles. From figure 11, it is evident that the capacitance values decrease on increasing the discharge-current loads. Non-uniform current-distribution in the porous matrix of the electrode is responsible for the capacitance degradation at higher discharge-current loads.^{27,28}

Capacitance values for the 12 V substrate-integrated lead-carbon hybrid ultracapacitors are sensitive to the test-protocol. Two-step-charge process, namely, constant-current charge followed by constant-voltage charge, is mandatory to fully charge the hybrid ultracapacitors. As the lead-carbon hybrid ultracapacitors comprise battery and carbon-based electrodes, the kinetics for both the electrodes happens to be quite different since the battery electrodes store energy in chemical reactants capable of producing charge while carbon-based electrodes store energy directly as physical charge-separation. The latter electrode displays fast kinetics owing to the non-faradaic ion adsorption-desorption processes in the electrical double-layer.²⁶ By contrast, battery electrodes fail to follow fast kinetics due to the governing faradaic charge-transfer processes,² and need longer time for full charge. Accordingly, it is not advisable to charge the hybrid ultracapacitors at constant-current for a longer time as it would cause evolution of gases at the electrodes due to water splitting from the aqueous electrolyte at higher voltages. Consequently, constant-voltage charge assists in fully charging the hybrid ultracapacitors.

Figure 11. Constant-current discharge data for 12 V substrate-integrated lead-carbon hybrid ultracapacitors in (a) AGM and (b) gel configurations.

During constant-voltage charge, the voltage for the hybrid ultracapacitors is kept below the water splitting over-voltage. In this study, the hybrid ultracapacitors are galvanostatically charged with 0.3 A current between 6 V and 13.8 V followed by potentiostatic charging at 13.8 V for 1 h. Capacitance values for the 12 V hybrid ultracapacitors in gel configuration is higher than the hybrid ultracapacitors in AGM configuration due to the enhancement of active surface-area of positive plates and the effect of polymeric structure of silica-gel on negative plates in the former.^{29,30}

To obtain energy-density value for the hybrid ultracapacitor, constant-power discharge experiments are mandatory to avoid the $(1/2) CV^2$ formalism, which is more appropriate for symmetric capacitors wherein no faradaic mechanisms are involved.³¹ Hybrid ultracapacitors are galvanostatically charged with 0.3 A current between 6 V and 13.8 V followed by potentiostatic charging at 13.8 V for 1 h. Hybrid ultracapacitors are subsequently discharged at constant-power loads

between 5 W and 25 W; the discharge profiles are shown in figure 12a and b for the hybrid ultracapacitors with AGM and gel configurations, respectively. Energy densities are the normalized values of energies with respect to the weight of hybrid ultracapacitors, whereas energies are obtained by multiplication of applied power and the discharge time. Power-density values for the hybrid ultracapacitors are calculated from the ratio of energy-density and response-time values.³² For calculation of energy and power densities, the applied power is chosen as 25 W, and the data are presented in table 1. It is noteworthy that AGM-based hybrid ultracapacitors behave like a power device, whereas gel-based devices behave more like an energy device. Non-uniform-current distributions are responsible for lesser release of stored-energy at higher discharge power-loads for both types of hybrid ultracapacitors.

Figure 12. Constant-power discharge data for 12 V substrate-integrated lead-carbon hybrid ultracapacitors in (a) AGM and (b) gel configurations

Self-discharge measurement is seminal for any energy-storage device. Self-discharge data-analysis for 12 V hybrid ultracapacitors are carried out after charging the devices at constant-voltage for 3 h at 13.2 V followed by 24 h open-circuit discharge at room temperature.³³ Self-discharge energy-loss factors (SDLFs) for the hybrid ultracapacitors are calculated from the voltage-loss data with respect to time from the relationship: $SDLF = 1 - (V/V_w)^2$, where V and V_w are the voltage after measured time and the working voltage. Voltage vs. time profiles for 12 V substrate-integrated lead-carbon hybrid ultracapacitors along with SDLF data are presented in figure 13. Self-discharge for the gel-based hybrid ultracapacitors is higher than the AGM-based hybrid ultracapacitors due to the higher electroactive surface-area of positive plates in the former. As the self-discharge is higher for gel-hybrid ultracapacitors, the leakage current for the hybrid ultracapacitors is also higher while the associated parallel resistance is lower. Leakage current for the hybrid ultracapacitors is measured during 24 h after fixing the voltage at 13.2 V at room temperature. Amperometric data for 12 V hybrid ultracapacitors obtained during leakage-current measurements are shown in figure 14. Parallel resistance after 24 h is estimated as a ratio of working voltage, i.e., 13.2 V, and leakage current after 24 h. Self-discharge, leakage-current and parallel-resistance data for AGM and gel-based substrate-integrated lead-carbon hybrid ultracapacitors are presented in table 1.³³

Pulse-cycle-life test data are collected over 100,000 charge at 3 A and discharge at 3 A pulses of 1 s duration, and capacitance values are measured after 10,000 pulse with 0.3 A discharge as shown in figure 15. Interestingly, both the AGM and gel-based hybrid

Figure 13. Self-discharge data for 12 V substrate-integrated lead-carbon hybrid ultracapacitors.

Figure 14. Current vs. time profiles for substrate-integrated lead-carbon hybrid ultracapacitors at 13.2 V for leakage current and parallel resistance measurements.

Figure 15. Pulsed cycle-life data for 12 V substrate-integrated lead-carbon hybrid ultracapacitors.

ultracapacitors exhibit little capacitance deterioration during repetitive cycling.

3.4 Cost comparisons between substrate-integrated lead-carbon hybrid ultracapacitors and commercially available ultracapacitors

The cost of commercially available ultracapacitors from Tecate,³⁴ Maxwell[®],³⁵ Axion Power[™],³⁶ Firefly[®] International Energy,³⁷ Nesscap³⁸ and VINA Tech³⁹ is ~20 US\$/Wh. Based on the bills of materials employed in the presently reported substrate-integrated lead-carbon hybrid ultracapacitors, their estimated cost is ~4 US\$/Wh. Performance data and cost comparison between commercially available ultracapacitors and substrate-integrated lead-carbon hybrid ultracapacitors reported in the present study are presented in table 2.²⁰

4. Conclusions

Cost-effective 12 V substrate-integrated lead-carbon hybrid ultracapacitors with flexible graphite sheets as negative current-collectors are reported. The problems associated with internal resistance of the negative current-collector and adhesivity of the activated-carbon layer to it, are mitigated by applying a thin poly-aniline coating on to the sheets. Both AGM and gel-based 12 V substrate-integrated lead-carbon hybrid ultracapacitors are performance tested using standard ultracapacitor-test-protocol, namely measuring their faradaic efficiency, internal-resistance values, response-time values, capacitance values, energy and power densities, self-discharge values, leakage currents, parallel-resistance values and cycle-life. A compelling feature of the lead-carbon hybrid ultracapacitor reported here is their low cost in relation to other commercially available ultracapacitors.

Table 2. Performance and cost comparison between commercially available ultracapacitors and substrate-integrated lead-carbon hybrid ultracapacitors.

	Commercially Available Ultracapacitors	Substrate-Integrated Lead-Carbon Hybrid Ultracapacitors
Cell Voltage / V	2.3–2.7	2–2.3
Charging Time / s	1–10	60–90
Energy Density / Wh kg ⁻¹	~5	~3
Power Density / W kg ⁻¹	Up to 10,000	Up to 5,000
Temperature range / °C	–40 to 65	–20 to 50
Maximum Cycle Number / Million	~1	~1
Cost / US\$/Wh	~20	~4

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