Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

Electrodeposited Polyethylenedioxythiophene with Infiltrated Gel Electrolyte Interface: A Close Contest of an All-Solid-State Supercapacitor with its Liquid-State Counterpart

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Weight calculation for the electro-deposited PEDOT

$$\mathbf{W} = \frac{\text{Charge passed (C)} * 142 \text{ (Mol. weight of EDOT)}}{96\,485 * 2.33 \text{ (no electron released per EDOT)}}$$

Calculations of specific capacitance of PEDOT from cyclic voltamatry and chrono charge-discharge methods.

Specific capacitance (F/g) of the PEDOT was calculated from the cyclic voltammogram using the following equation [1]**.**

$$\mathbf{C = 2*} \frac{Q}{(E_1\text{-}E_2)m} \text{ ---------- (1)}$$

$Q(\text{charge}) = \frac{\int_{E1}^{E2} I(E)dE}{v}$, is the average charge obtained by the integration of cathodic and anodic parts of the voltammogram

E_1-E_2 = Potential window (1 V)

m = Weight of the PEDOT coated in one of the electrodes (g)

v = Scan rate (mV s^{-1})

Specific capacitance (F g^{-1}) of the material was also calculated from the charge-discharge experiments using the following equation:

$$\mathbf{C} = 2*\left(\frac{I\Delta t}{\Delta V*M}\right) \text{ ---------- (2)}$$

Δt = Discharge time
Δv = Potential window
I = Constant current used for charging and discharging
M = Weight of active electrode material in one of the electrode.

- As the experiments are done in symmetrical 2-electrode fashion, *i.e.* capacitance of the cell will be the half of the single electrode capacitance, multiplication of the capacitance by a factor of 2 is included in the above equations.
- Contribution of carbon paper towards the capacitance is negligible and not considered for the calculations.
- Volumetric capacitance (F cm^{-3}) calculated by dividing the single PEDOT electrode capacitance by volume active area (0.03 cm^3).
- Areal capacitances (F cm^{-2}) calculated by dividing the single PEDOT electrode capacitance by area (1 cm^2).
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Energy density (E_d) and power density (P_d) for the whole device were calculated from the capacitance value obtained from the charge-discharge method.

Volumetric Energy density $E_V \left(\text{Wh cm}^{-3}\right) = \frac{1}{2} * \frac{C_V V^2}{3600}$

C_V (F) = Volumetric capacitance for the whole device calculated from charge-discharge method

V= Voltage window

Volumetric Power density P_v (W cm^{-3}) $= \frac{E_v}{t}$

t = Discharge time in hour calculated from the discharge curve

Gravimetric energy density (E_d) and power density (P_d) were calculated from the capacitance value obtained from the charge-discharge method

Energy density $E_d \left(\text{Wh Kg}^{-1}\right) = \frac{1}{8} C_s V^2 * \frac{1000}{3600}$

C_s = Specific capacitance of PEDOT calculated by charge-discharge (F/g)

Power density P_d (W Kg^{-1}) $= \frac{E_d}{t}$

V= Voltage window

t = Discharge time in hour calculated from the discharge curve

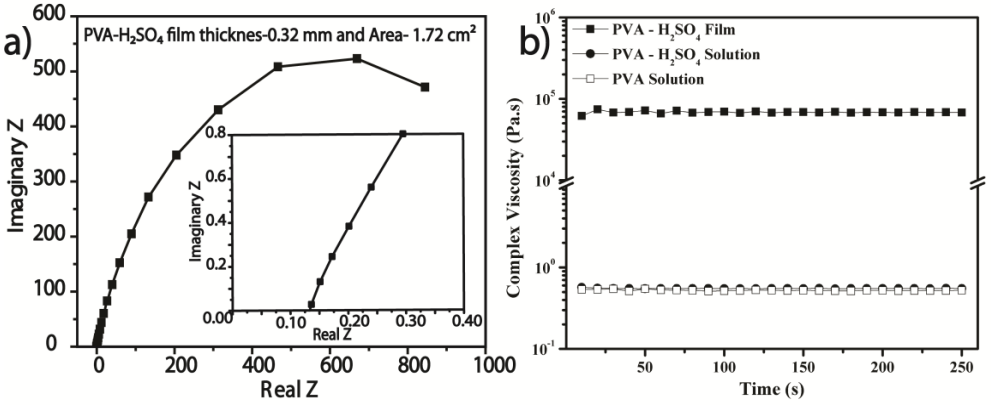

Figure S1: a) Impedance analysis of PVA-H_2SO_4 film. Films show a conductvity 0.14 S/cm. b) Complex viscosity measurment of various solutions and samples.

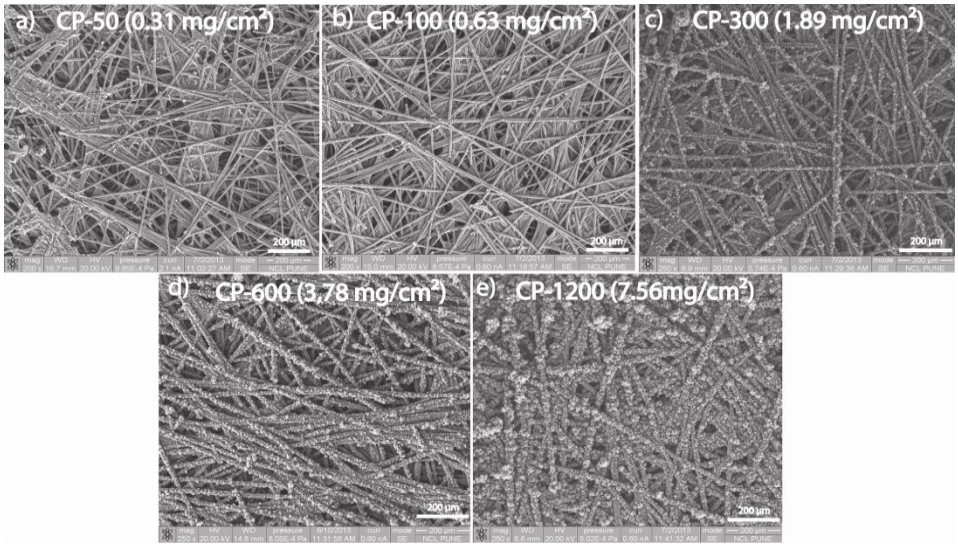

Figure S2.Comparitive SEM images of the PEDOT coated carbon papers: a) CP-50, b) CP-100, c) CP-300, d) CP-600 and e) CP-1200.

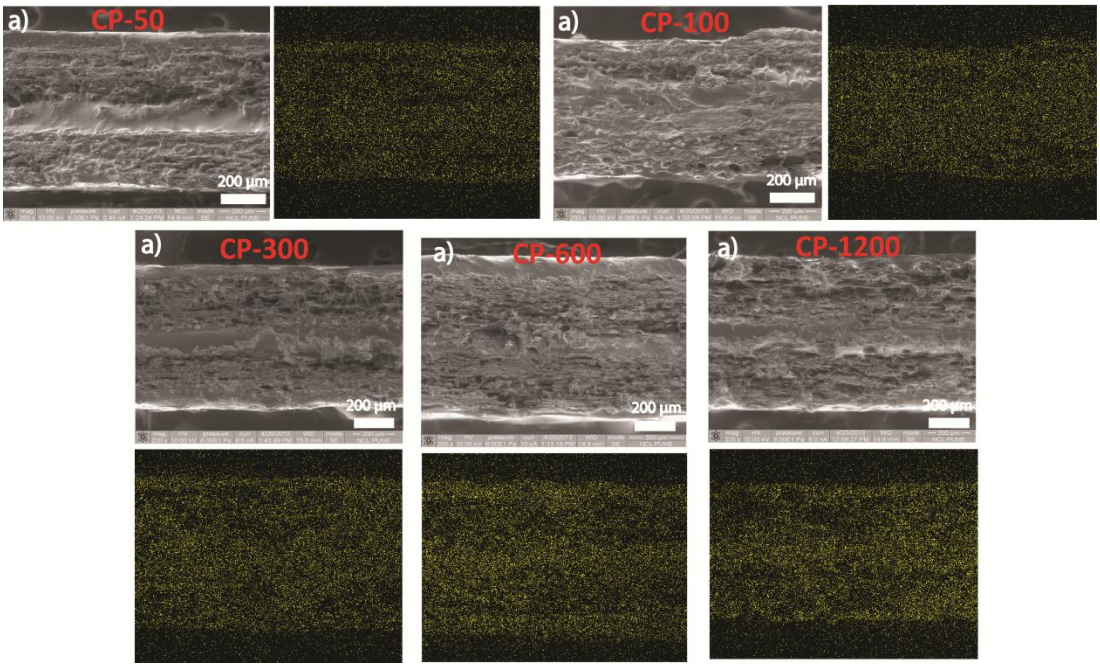

Figure S3. Comparative cross-sectional SEM images and the corresponding S mapping (in the right side of each SEM images) of the solid devices made from, a) CP-50, b) CP-100, c) CP-300, d) CP-600 and e) CP-1200.

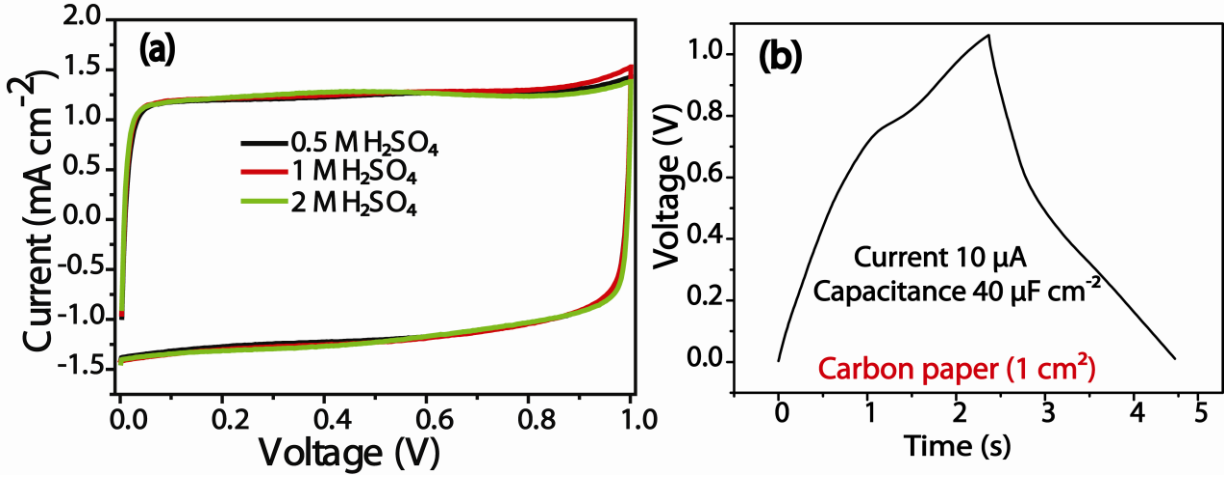

Figure S4: a) Cyclic voltamogram of CP-300 in different concentration sulphuric acid b) Charge-discharge profile of bare carbon paper in 2-electrode method in 0.5 M H_2SO_4.

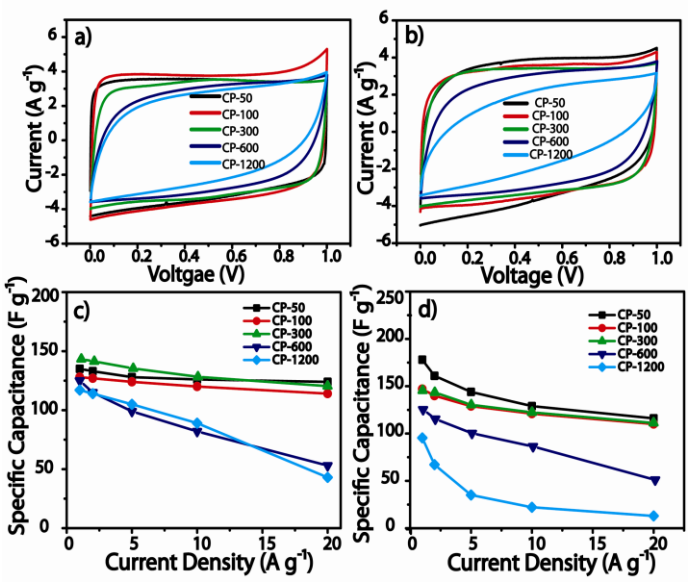

Figure S5: Cyclic voltammograms of PEDOT coated carbon paper for different time of deposition carried out at a scan rate of 50 mV s^{-1}: a) in 0.5 M H_2SO_4, b) using PVA-H_2SO_4. The corresponding specific capacitance *vs*. current density plots of the samples are given in c) and d), respectively.

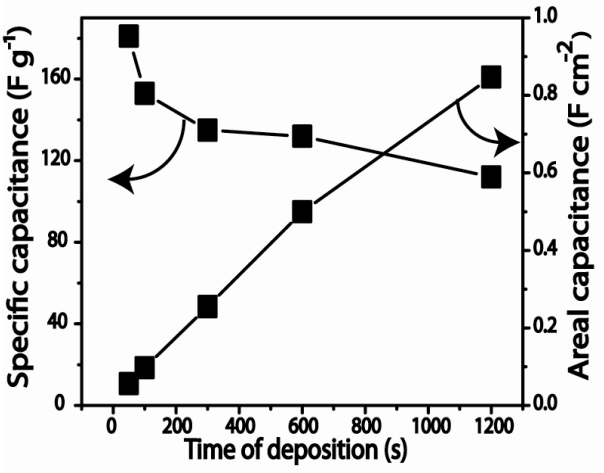

Figure S6: Specific capacitance variations of PEDOT with areal capacitance; capacitance values of each electrode are measured at 0.5 A g^{-1} current density.

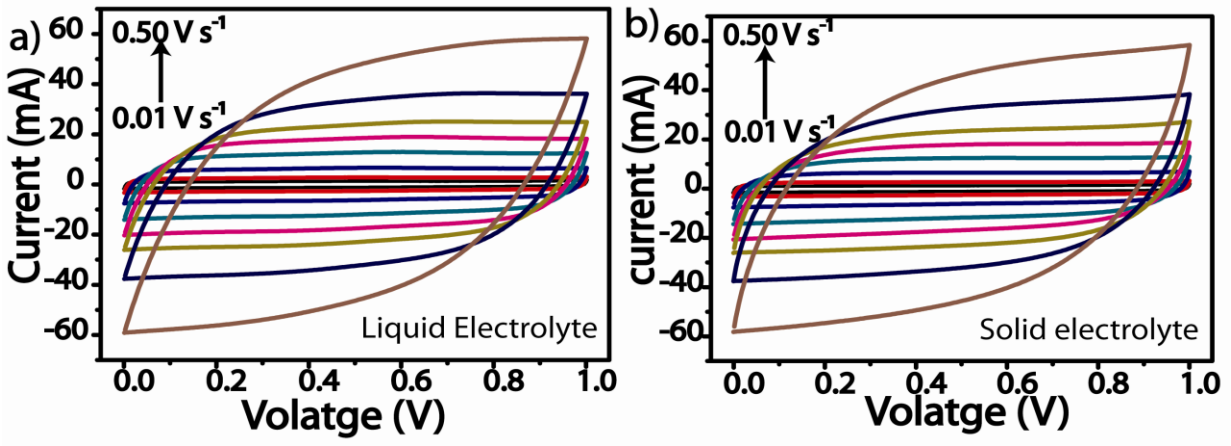

Figure S7: Cyclic voltammograms of CP-300 at various scan rates: a) in 0.5 M H_2SO_4, b) using PVA-H_2SO_4.

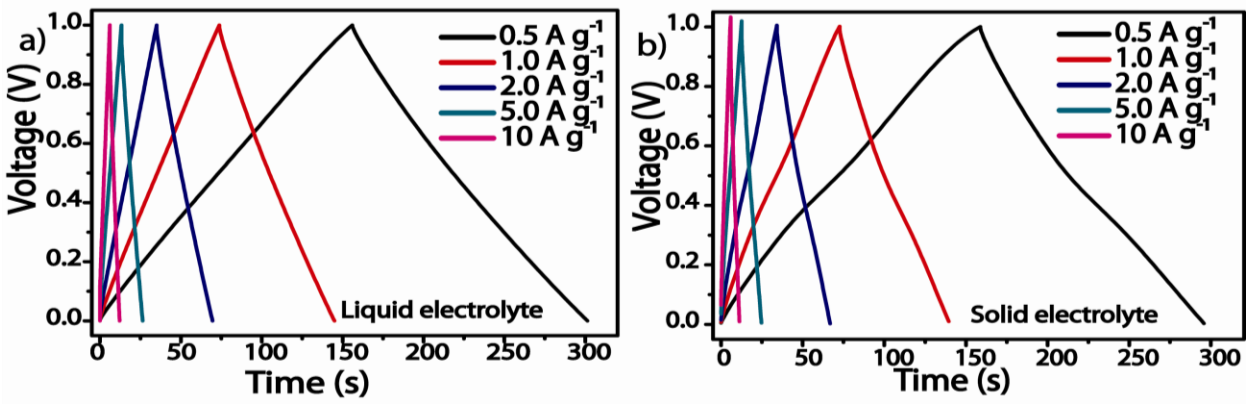

Figure S8: Chrono charge-discharge profiles of CP-300 at various current densities: a) in 0.5 M H_2SO_4, b) using PVA-H_2SO_4.

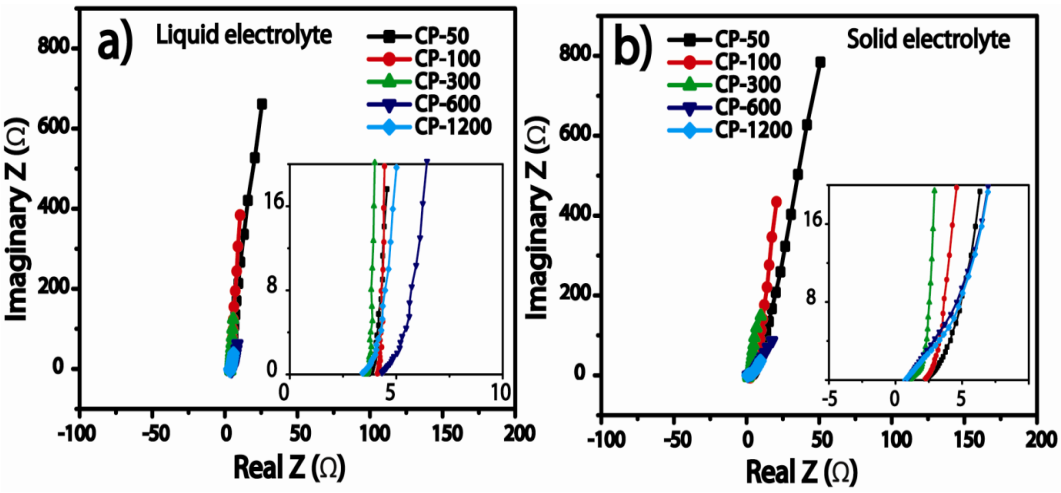

Figure S9: Nyquist plots of the PEDOT coated carbon paper corresponding to the different deposition times: a) in 0.5 M H_2SO_4, b) using PVA-H_2SO_4.

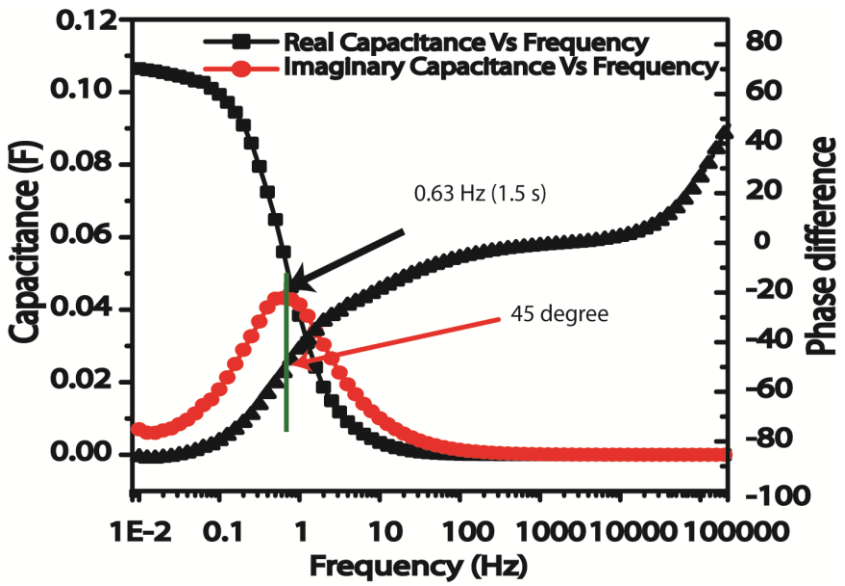

Figure S10 : Frequency dependant imaginary and real capacitances and phase difference of CP-300 in PVA-H_2SO_4.

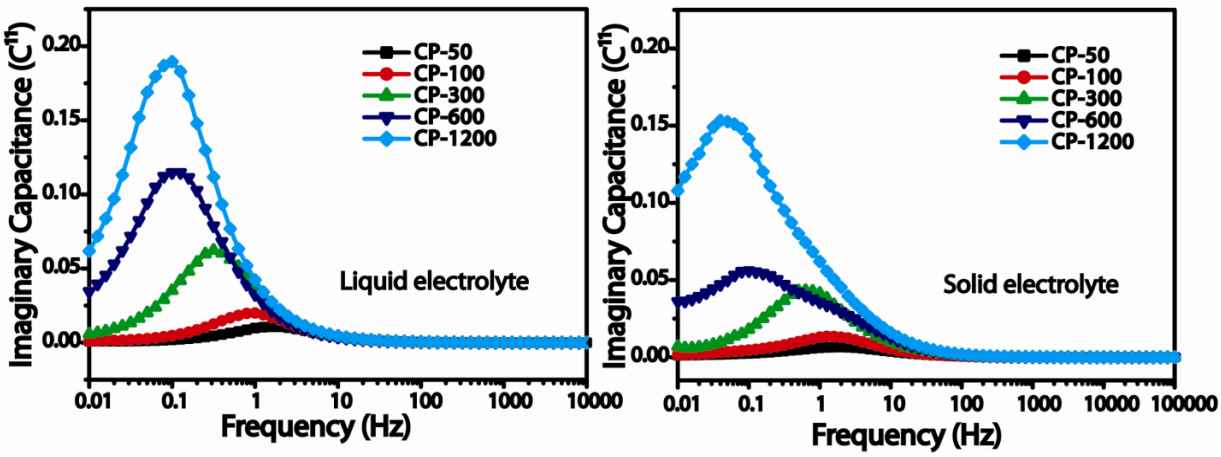

Figure S11: Frequency dependent imaginary capacitance of PEDOT coated carbon paper for different time of deposition: a) in 0.5 M H_2SO_4 b) using PVA-H_2SO_4.

Impedance phase angle of CP-300 in both the phases is shown in **Figure S10**. This clearly dictates the nature of the charge storage properties with the frequency. Normally, at the high frequency region, a supercapacitor will show resistive nature with 0 phase lag between voltage and current and at low frequency region it will show a -90 degree phase lag. Here, the nature of the phase angle with frequency is similar in both cases of liquid and solid electrolyte

and it reaches nearly -90^{o} at low frequency showing ideal capacitive nature in both cases (**Figure 6c**). This explains why similar capacitive retention is obtained in liquid and solid electrolyte with the faster rate. As that of impedance, complex form of frequency dependent capacitance can be defined in terms of real capacitance(C^{I}) and imaginary capacitance (C^{II}) as follows [2-4].

$$C(w) = C^{I}(w) + C^{II}(w)$$

where

$$C^{I}\ (w) = \frac{Z^{II}(W)}{\omega|Z(w)|^{2}}$$

$$C^{II}\ (w) = \frac{Z^{I}(W)}{\omega|Z(w)|^{2}}$$

$$Where\ |Z(w)|^{2} = Z(w)'^{2} + Z(w)"^{2}$$

The real part of the cell capacitance calculated from the impedance analysis matches with the CV and charge-discharge method. At 0.01 Hz, CP-300 shows a capacitance of 116 F g^{-1} with a phase angle of -90^{o} shown in the plot of frequency *vs* capacitance (**Figure S10**). The imaginary part of the capacitance, on the other hand, depicts the energy lost during the charge-discharge cycle. A plot of imaginary capacitance *vs*. frequency will have a maximum, normally happens at -45^{o} phase angle and the corresponding frequency is called the relaxation frequency (**Figure S10**). Comparative plots are given in **Figure S11** for the systems based on the solid and liquid electrolytes. The inverse of the above frequency is called the time constant which measures the kinetics of the capacitor and is known to be as 'figure of merit of a capacitor'. Another method to calculate the time constant is the inverse of the frequency at which phase difference is -45^{o} (**Figure S10**). In both methods CP-300 shows a time constant of 1.5 seconds.

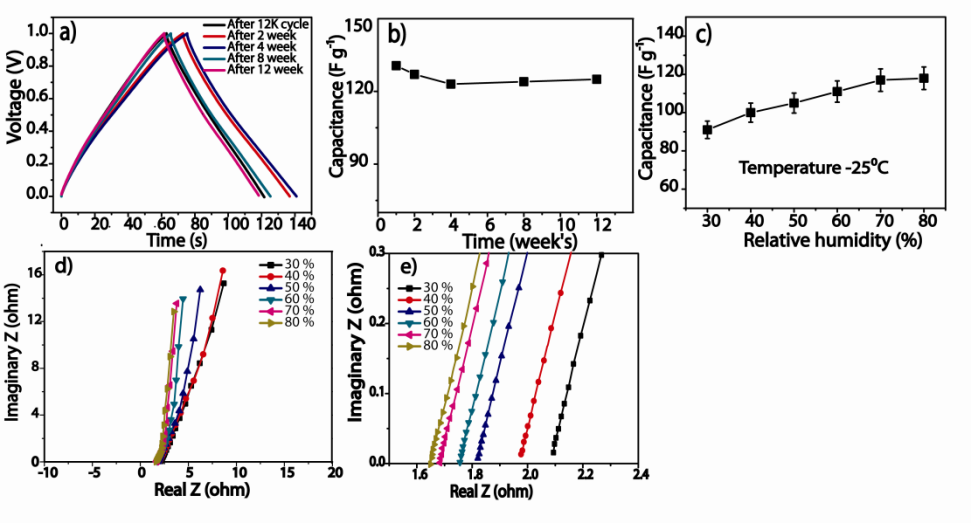

Figure S12: a) Charge-discharge profiles taken at 0.5 A g^{-1} during different time intervals, b) the capacitance values calculated from the charge-discharge plots taken at different time intervals, c) humidity dependent capacitance of PEDOT in the solid-state device based on CP-300, d) Nyquist plots taken under different humidity conditions for the solid-state device based on CP-300, e) the zoomed high frequency region of the Nyquist plot as given in 'e'.

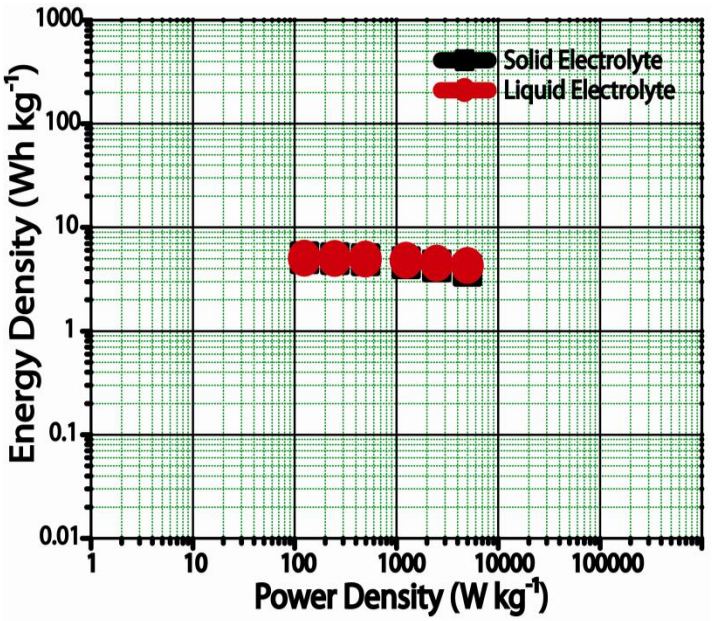

Figure S13: Ragone plot of CP-300 depicting the garvemetric energy density *vs* power density.

Table S1. Total specific capacitance obtained from the solid-state devices including the weight of the current collector and carbon paper.

Samble	Loading of PEDOT (mg)	Weight of Carbon paper (mg)	Total weight of device (mg, ± 5%)	Capacitance obtained mF	Capacitance of the device (F g^{-1}, ±5%)
CP-50	0.63	13	45	28.5	0.6
CP-100	2.52	13	46	48.2	1.0
CP-300	3.78	13	47	127.6	2.7
CP-600	7.56	13	51	249.5	4.9
CP-1200	15.12	13	59	419.6	7.1

Table S2 4-probe electrical conductvity data of the PEDOT coated carbon paper.

Sample	Conductivity (S cm^{-1})
CP-100	142
CP-300	154
CP-600	162
CP-1200	179

It is clear from Table S2 that, with the increase in the amount of PEDOT, conductivity of the carbon strip is increasing (from 142 S cm^{-1} to 179 S cm^{-1}). As more amount of conducting PEDOT is filled inside the pores of the porous paper by electro-deposition, it leads to better connectivity between the individual carbon fibers. Better interconnectivity between the fibers decreases the contact resistance and leads to high conductivity. However, the conductivity enhancement achieved by the higher mass loading of PEDOT brings in restrictions to

concomitantly establish the electrode-electrolyte interface as pore-filling by PEDOT can reduce the accessible channels for the gel electrolyte. This leads to lowering of capacitance in the case of CP-1200, which has higher mass loading of PEDOT, even though it possesses high conductivity.

References

1. Chen, W.; Fan, Z.; Gu, L.; Bao, X.; Wang, C., *Chem. Commun.* **2010,** 46, 3905-3907.
2. Taberna, P. L.; Portet, C.; Simon, P., *Appl. Phys. A* **2006,** 82, 639-646.
3. Taberna, P. L.; Simon, P.; Fauvarque , J. F., *J. Electrochem. Soc.* **2003,** 150, A292-A300.
4. Miller, J. R.; Outlaw, R. A.; Holloway, B. C., *Science* **2010,** 329, 1637-1639.