Negative Capacitance Based on Isomeric Polythiophene in Action

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Why capacitance enhancement (S1):

Ferroelectric materials are well known for their ability to exhibit NC characteristic and it is due to the presence of spontaneous polarization that can be reversed on applying the electric field. NC characteristic exhibited by ferroelectrics is unstable and quickly relaxes to the positive capacitance leading to the inherent Q-V hysteresis.

The electrostatic energy density of a dielectric material is described by the following general

equation
$$W= \int_{0}^{D} E\langle D \rangle \, dD$$
------- (1)

Where E is the applied electric field and D is the displacement field, In a similar way the amount of electrostatic energy stored in a capacitor is given by the following equation

$$W = \int_{0}^{Q} V\langle Q \rangle \, dQ$$
--------(2)   where Q is the electrode

charge and V is the applied potential. In a capacitor the amount of energy stored is corresponding to the area above the Q vs V curve as being depicted in **figure 1A**. Positive capacitors are being characterized by their linear Q-V characteristic For a regular positive capacitor having constant capacitance C the total energy stored ($W= 1/2CV^2$) is depend on the breakdown voltage and dielectric permittivity of the dielectric material. In contrast to positive capacitor in negative capacitance material the Q-V characteristic cannot be linear for all applied

voltages (**figure 1B**). NC feature is unstable in isolation however it get stabilized in combination with positive capacitance material[1]. NC feature can be described by using 3rd order polynomial.

$$V = a (Q - dQ) + b (Q - dQ)^3 \qquad \text{------ (3)}$$

where a<0, b>0 and dQ is remanent charge.

Owing to inherent Q-V hysteresis NC materials are not suitable for the energy storage application. As the area inside the hysteresis loop corresponding to the amount of energy dissipated (W_{loss}). However, if we combine a positive capacitance material (V=Q/C) with NC material being described by the equation (3) in series, we can write the following V-Q relationship for whole system.

$$V = (1/C + a) Q - adQ + b(Q - dQ)^3 \qquad \text{------ (4)}$$

In combined capacitor system (NC: PC), under specific condition when 1/C> -a, there should be no Q-V hysteresis to achieve energy storage efficiency equal to one. Owing to the positive curvature in the non-linear Q-V curve (**figure 1C**) of combined capacitor system the total energy density enhances as compare to the linear positive capacitor alone, even at identical voltage and stored charge. From eq. 2 and 4 the energy stored in such a combined capacitor system can be given by the following equation.

$$W = (1/2C - a) Q^2 - bdQQ^3 + b/4Q^4 \qquad \text{-------- (5)}$$

Due to positive curvature in non-linear Q-V characteristic, series combination of NC material with PC material enhances the total capacitance and hence energy storage. Along with this series arrangement of NC layer also reduces the overall leakage current through the capacitor and enhances the breakdown voltage. Hence NC layer incorporation avail to apply higher voltage as compare to regular capacitor alone leading to considerably high energy density
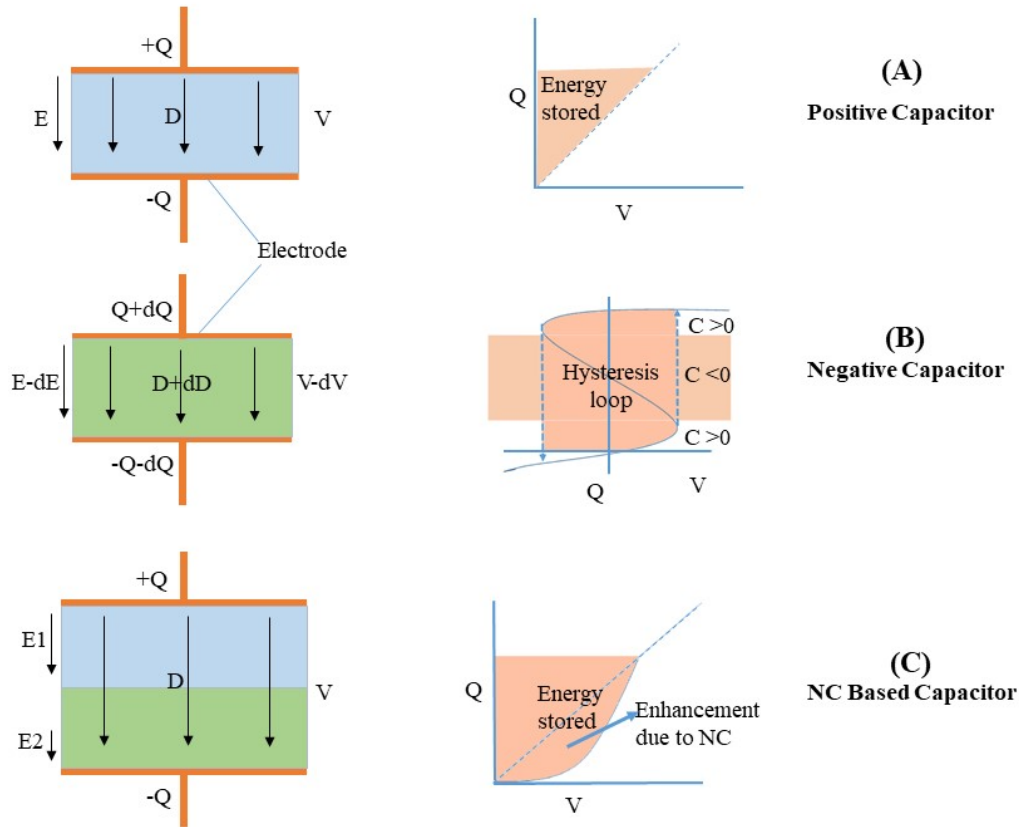
Figure 1: Effect of series arrangement of positive and negative capacitance to enhance energy storage. **A)** Positive capacitor with charge (*Q*), voltage (*V*), electric field (*E*), and displacement field (*D)*. Energy stored is area above the *Q–V* curve. **B)** Capacitor with negative differential capacitance d*Q*/d*V* < 0 due to d*D*/d*E* < 0. Exhibiting Q-V hysteresis, energy loss (orange area). **C)** Series arrangement of NC and positive capacitance to create an NC supercapacitor with improved energy storage and without hysteresis.

Spontaneous polarization P in ferroelectric material induces the bound charges at interfaces. If not compensated bound charges exerted an electric field in the direction opposite to P, hence termed as depolarization field. Depolarization field results into an increase in electrostatic energy in ferroelectric material called as depolarization energy. When a positive voltage is applied across a metal-ferroelectric-dielectric-metal (MFIM) hetero-structure this causes build-up of charge density (dQ) at the metal plates as well as the magnitude of spontaneous polarization P in ferroelectric. this corresponds to the positive capacitance (dQ/dV >0) of whole

stack. However, increase in P of ferroelectric leads to decrease in free energy due to double well shaped free energy landscape and simultaneously increase in depolarization energy. Within a certain region the decrease in free energy is higher than increase in depolarization energy and hence total ferroelectric energy decreases with increasing P. In this scenario the total energy in dielectric layer is sum of the energy supplied from the external voltage source and decrease in ferroelectric energy. In other word there is a transfer of energy from ferroelectric layer to dielectric layer resulting enhanced energy in dielectric beyond supplied from voltage source.[2] In this case at the same applied voltage the dielectric layer in MFIM stack experienced high displacement field than in stand-alone situation. The higher displacement field in dielectric layer corresponds to the high potential across the dielectric layer (V_{DE}) which is larger than applied voltage (V_A). This also results into the internal potential amplification ($dV_{int}/ dV_A >0$). In this scenario the charge response (dQ/dV) which corresponds to the total capacitance of MFIM hetero-structure (C_{FE-DE}) is larger than the dielectric layer(C_{DE}) alone. Such capacitance enhancement which is the resultant of NC feature of ferroelectric material arises only when the condition ($d^2U/dQ^2<0$) is being satisfied, means the total energy of ferroelectric material decreases. Since NC feature of ferroelectric material is responsible for capacitance enhancement. So, it is thought that the mechanism responsible for the capacitance enhancement in IPTh-IPTh-I_2 system is to be the same as in FE-DE hetero-structure.

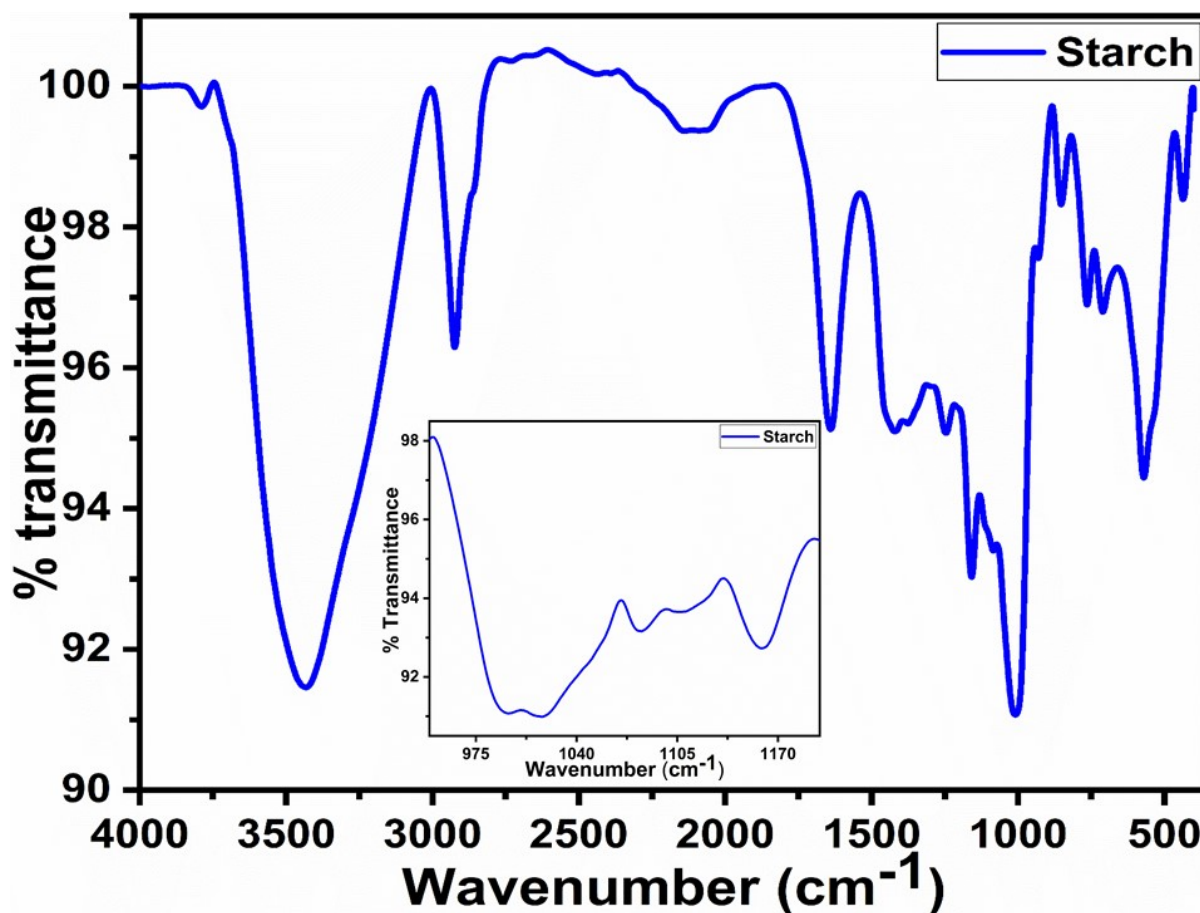**Characterization of starch & paper (S2):**

Figure 2: FTIR spectrum of starch

Figure 2 exhibits FTIR spectrum of starch. As starch is the polymer of glucose in which glucose units are connected to one another by α-1,4 and α-1,6 glycosidic linkage leading to both linear and branched chain. The vibrational band observed at 3428 cm^{-1} corresponding to the O-H stretching. Band observed at 2931 cm^{-1} and a weak shoulder at 2861 cm^{-1} are due to asymmetric and symmetric C-H stretching vibration respectively. O-H bending band of absorbed moisture is observed at 1629 cm^{-1}. Weak intensity band observed at 1420 and 1377 cm^{-1} are due to the asymmetric and symmetric C-H bending vibration respectively. In-plane C-OH deformation band observed at 1250 cm^{-1}. Weak intensity bands appear at 1160 and 1108 cm^{-1} corresponds to C-O-C glycosidic linkage and C-O ring stretching respectively. Bands appears at 1059 and 1030 cm^{-1} are due to C-OH stretching of 2° and 1° alcohol respectively. Several band observed

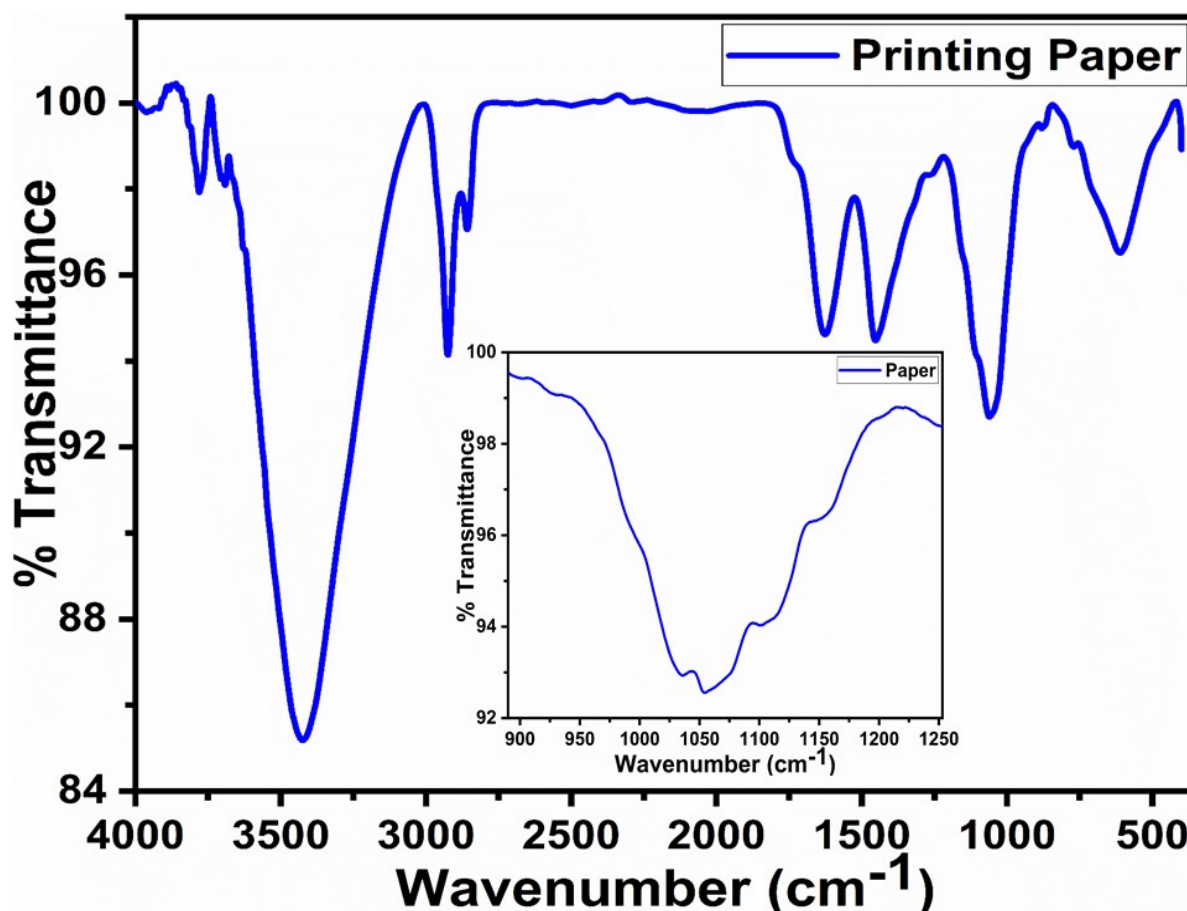below 900 cm^{-1} are due to C-C-C, C-C-O, C-O-C, O-C-O and C-OH deformation of glucose ring present in starch.

Figure 3: FTIR spectrum of paper

Figure 3 represented the FTIR spectrum of printing paper. As cellulose is the chief component of paper which in turn is the linear polymer of glucose in which glucose units are connected or bonded to each other by β-1,4 glycosidic linkages. Broad band observed at 3432 cm^{-1} is due to the O-H stretching vibration. Bands at 2928 and 2852 cm^{-1} is due to asymmetric and symmetric C-H stretching. O-H bending vibration of absorbed moisture is observed at 1628 cm^{-1}. Asymmetric C-H deformation band observed at 1465 cm^{-1}. Vibrational bands of low intensity observed at 1146 and 1110 cm^{-1} is due to the presence of C-O-C glycosidic linkage and C-O ring stretching respectively. Band at 1054 cm^{-1} is due to C-OH stretching vibration. Vibration band observed at 704 cm^{-1} corresponding to C-O-C deformation band. Weak intensity band observed as shoulder at 613 cm^{-1} is due to the C-C-C bending vibration.
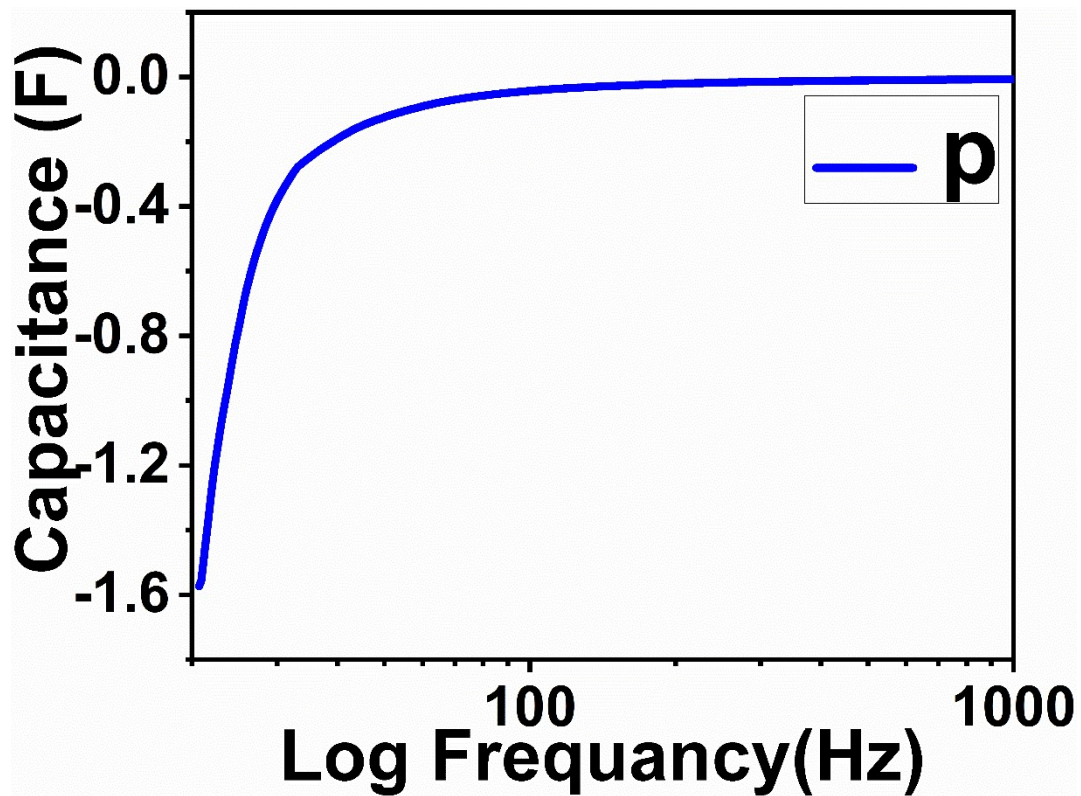
Figure 4: NC of p-doped (I_2-doped) IPTh-I_2

Figure 4 exhibits the negative capacitance of IPTh-I_2 at 25 °C and 1V applied potential. Negative capacitance value decreases with increasing applied field frequency and become positive at field frequency of >3KHz and at field frequency above 1KHz the value become too small to be suitable for SCs fabrications.

References:

[1] M. Hoffmann, F. P. G. Fengler, B. Max, U. Schroeder, S. Slesazeck, T. Mikolajick, Adv. Energy Mater., 2019, **9**(40), 1901154.

[2] A. K. Saha, S. K. Gupta, J. Appl. Phys., 2021, **129**, 080901