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Electronic Supporting Information

Elucidating the Role of Copper as Redox Additive and Dopant on the Performance of PANI based Supercapacitor

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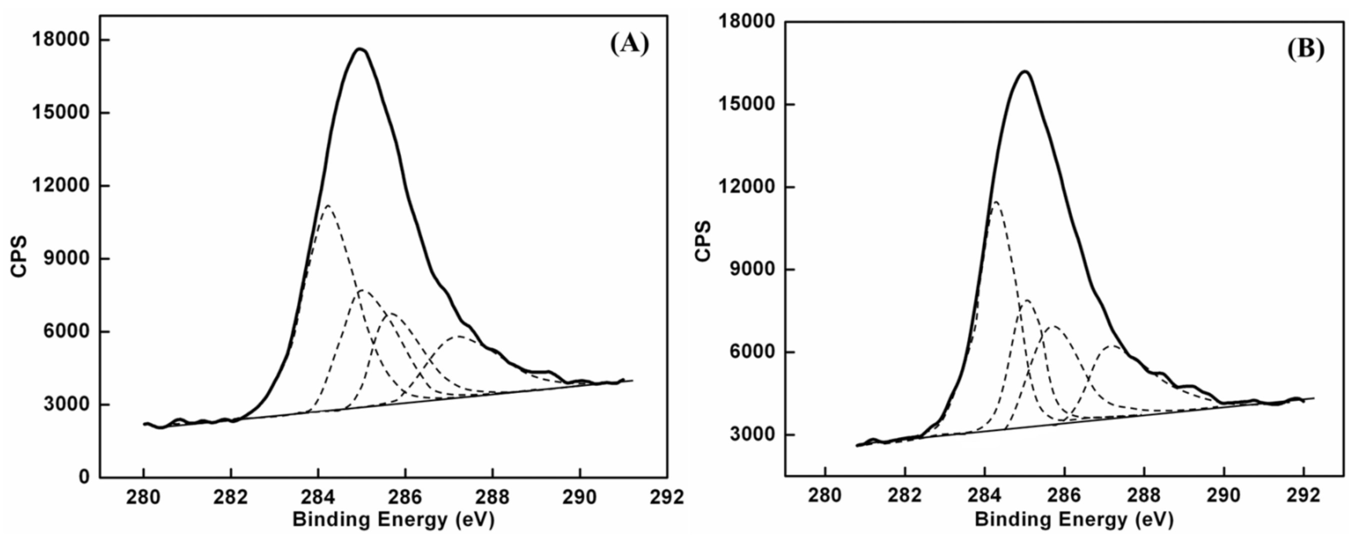

Fig. S1 XPS narrow scans of (A) PANI and (B) Cu-PANI for C 1s. The raw data has been deconvoluted into Gaussian peaks.

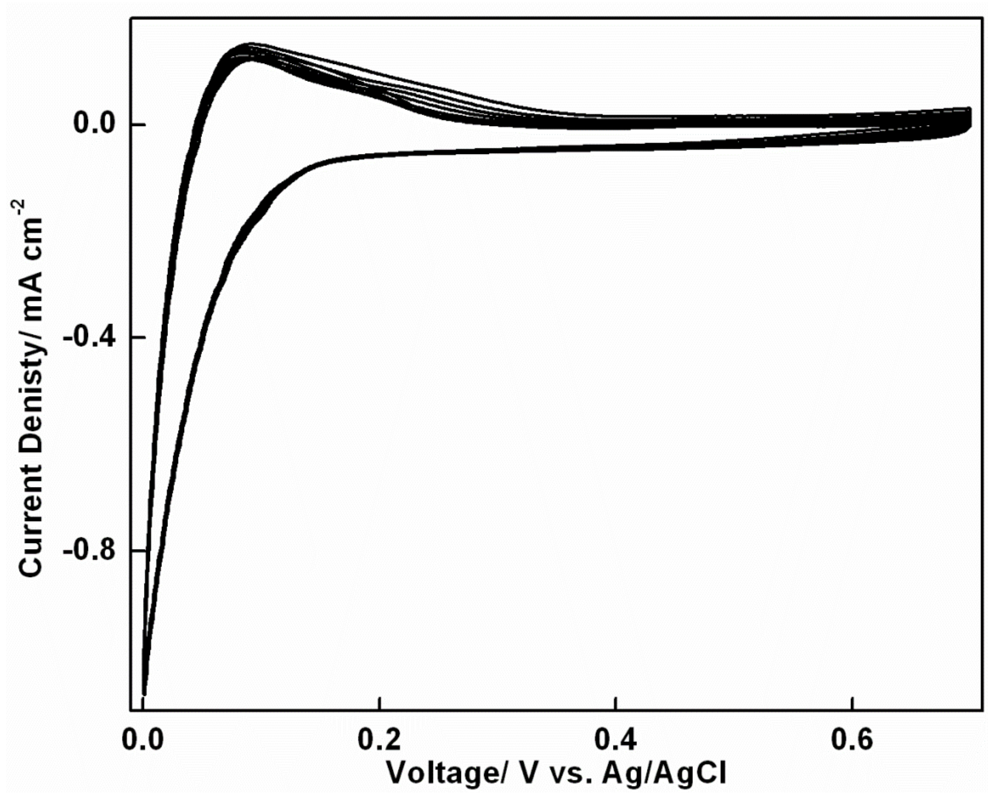

Fig. S2 Cyclic voltammogram of FTO electrode in H_2SO_4+$CuSO_4$ electrolyte

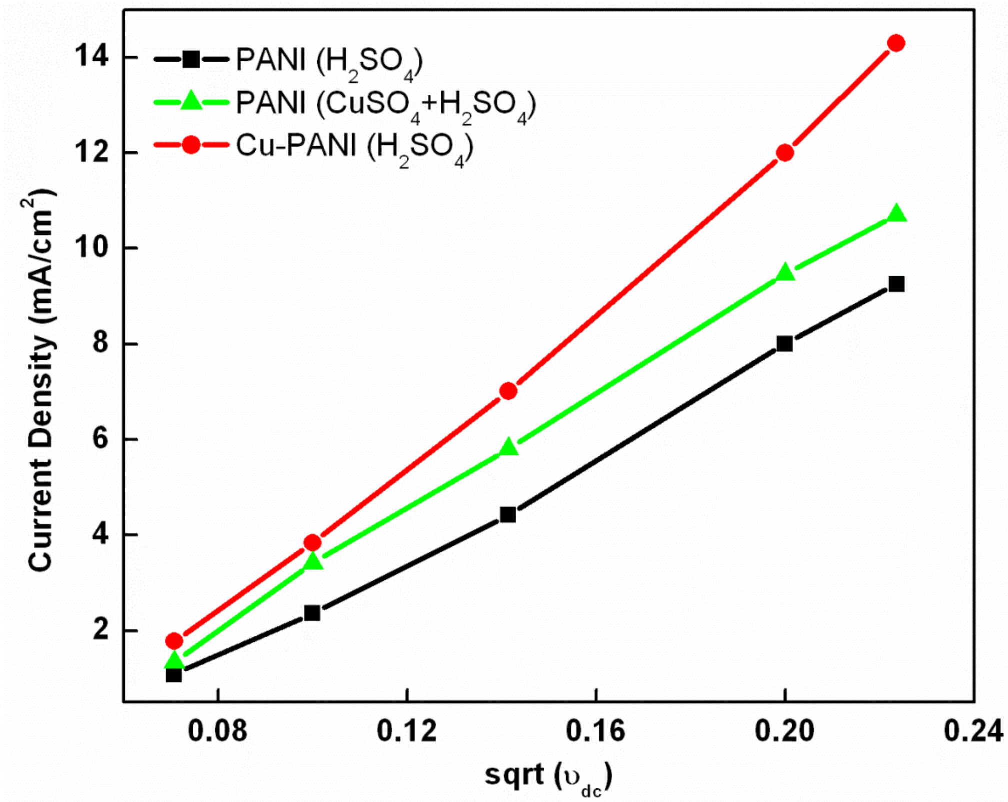

Fig. S3 Linear profile of current with square root of scan rate for all the samples under consideration

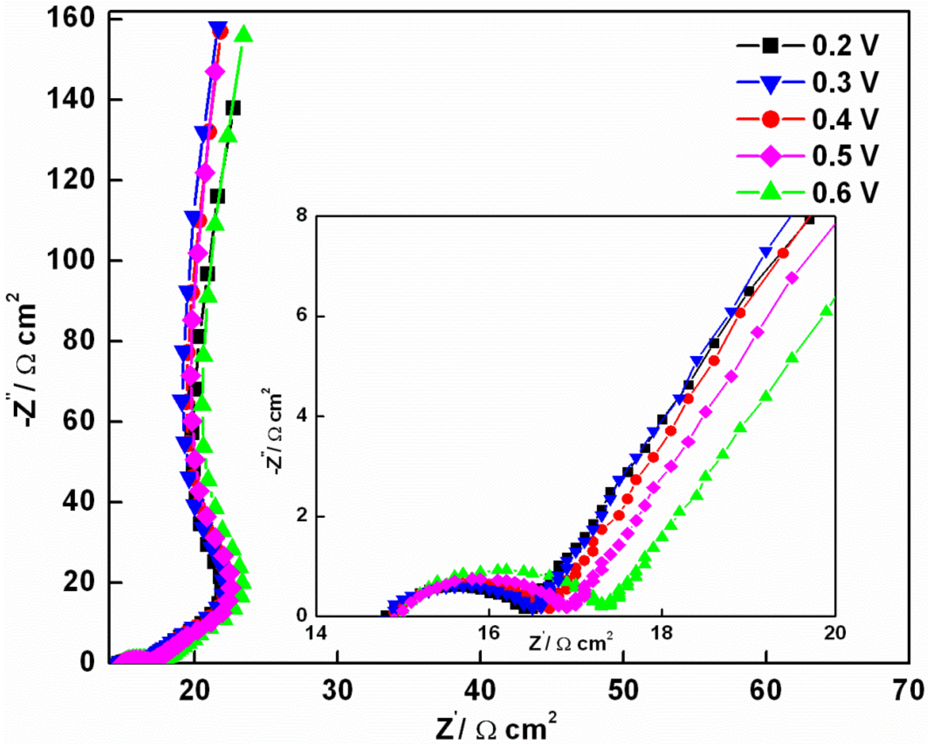

Fig. S4 Nyquist plot of PANI (H_2SO_4) at different applied potentials

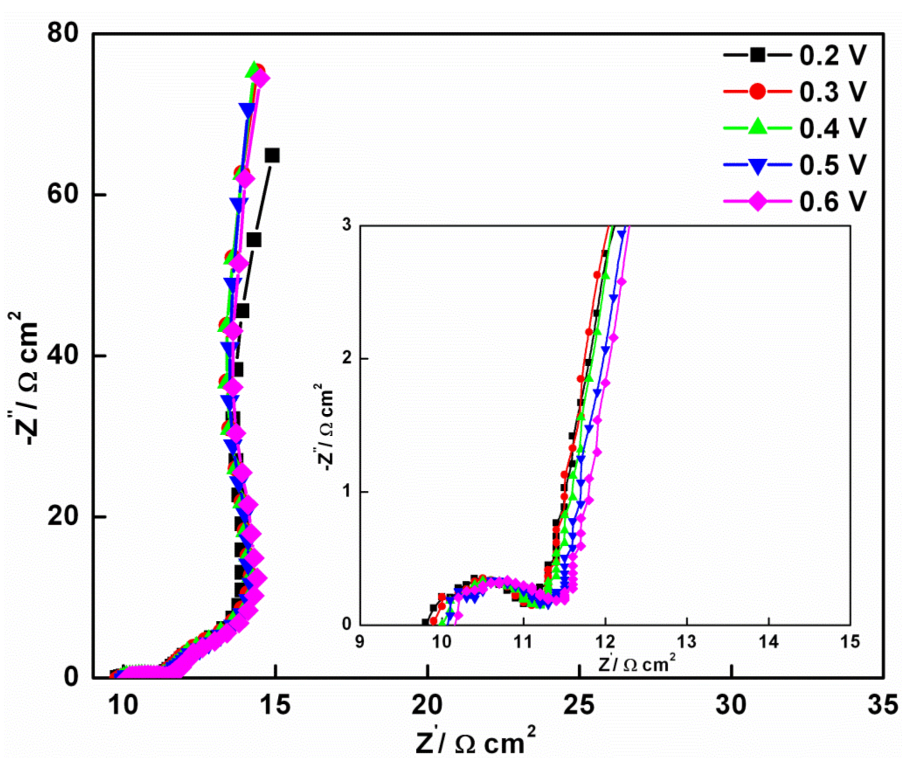

Fig. S5 Nyquist plot of Cu-PANI (H_2SO_4) at different applied potentials

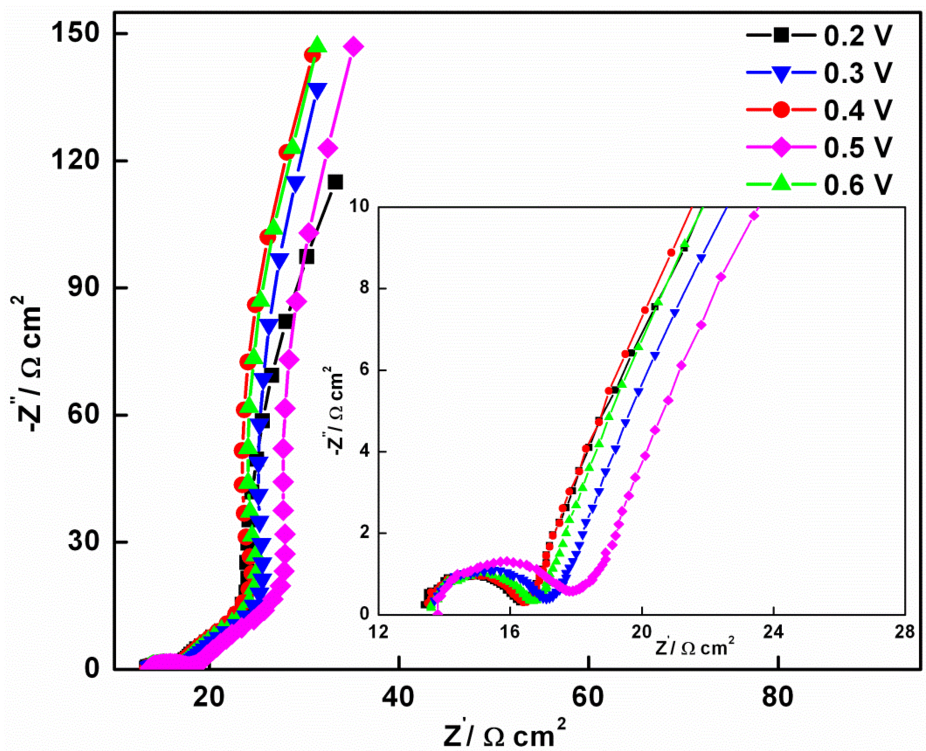

Fig. S6 Nyquist plot of PANI ($CuSO_4$+H_2SO_4) at different applied potentials

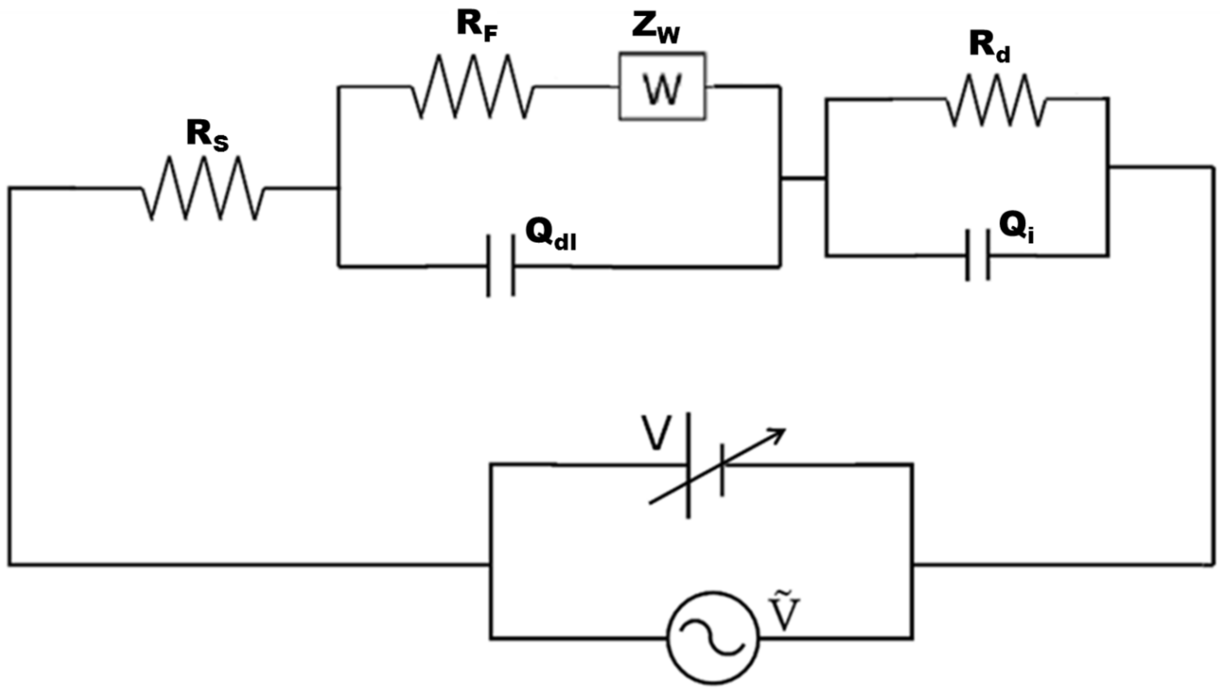

Fig. S7 Equivalent circuit employed for faradically active and spatially inhomogeneous interfaces of electrode – electrolyte systems

Simulation for C' vs. frequency

The simulation of C' vs. frequency is done using $C = {}^{\kappa\sigma}\big/_{Im^*\,\omega(\kappa+\sigma)L}$, where Im^* is derived from the imaginary part of complex impedance (Z) given by Eq. (S1),

$$Z = \frac{2\gamma}{(1+\gamma)^2\sqrt{j\omega^*}\,sinh\left(\sqrt{j\omega^*}\right)} + \frac{(1+\gamma)^2 coth\left(\sqrt{j\omega^*}\right)}{(1+\gamma)^2\sqrt{j\omega^*}} + \frac{\gamma}{(1+\gamma)^2}$$

(S1)

where, ω is the angular frequency, ω* $\left(\sqrt{\omega ACL^2(\kappa+\sigma)/2\kappa\sigma}\right)$ is the dimensionless angular frequency, A is cross-sectional area of the electrode, C is capacitance per interfacial area, L is the thickness of electrode, γ is the ratio of solution to matrix phase condcutivity, σ is matrix phase conductivity and κ is effective conductivity of the electrolyte in the electrode. For γ =0, the real and imaginary parts of Eq. (S1) collapse to Eq. (S2) and Eq. (S3) derived by Motupally et al.[1] for the impedance response of a diffusion-limited process.

$$Re = \frac{W_0}{\sqrt{\omega}}\left\{\frac{\sinh(\psi) - \sin(\psi)}{\cosh(\psi) - \cos(\psi)}\right\} \tag{S2}$$

$$Im = \frac{-W_0}{\sqrt{\omega}}\left\{\frac{\sinh(\psi) + \sin(\psi)}{\cosh(\psi) - \cos(\psi)}\right\} \tag{S3}$$

where $\psi = \sqrt{2\omega L^2/D}$, D is the diffusion coefficient and W_0 is the warburg coefficient. The behaviour of modified impedance is characterized by three distinct regions, viz. the semi-infinite diffusion (high frequency), transition (mid frequency), and finite diffusion (low frequency) regions. The frequency range in which the three regions are observed is controlled by the values of diffusion coefficient and the thickness of the film.

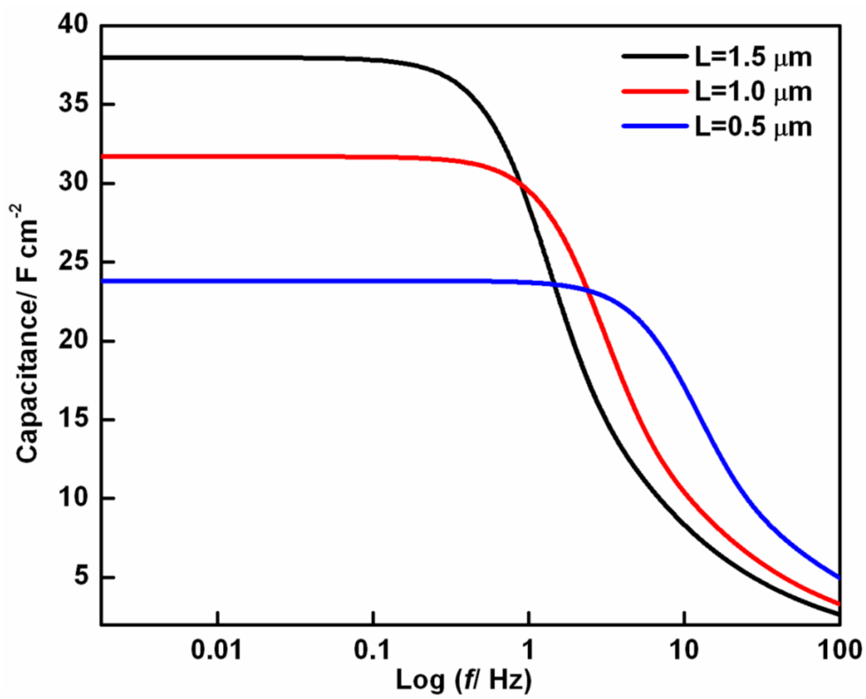

Fig. S8 Simulated capacitance vs. frequency plot as a function of electrode thickness

Fig. S8 represents the simulated Capacitance vs. frequency plot for $D = 1 \times 10^{-9}\ cm^2 s^{-1}$, $W_0\ and\ R_{ct} =\ 8\ \Omega/s^{0.5}$ and $22\ \Omega$, respectively with two distinguishing features: (1) At low frequency, $\omega \ll\ D/L^2$ the phase angle tends to infinity and a vertical line region perpendicular to the real axis is seen on a Nyquist plot. In this region, the diffusion behavior is limited by the finite length of the film and a higher capacitive effect is observed due to charge saturation. The thicker electrode leads to the increase in fraction of total device mass and thus capacitance increases[2] at this frequency and (2) At higher frequencies, $\omega \gg\ D/L^2$ the hyperbolic cotangent term tends to unity and the non-uniform utilization of current becomes more prominent for thicker electrode which causes a decrease in the value of effective capacitance. In this frequency region, thinner electrode leads to a higher capacitance. At intermediate frequencies when $\omega \approx\ D/L^2$,a transition from high capacitance to low capacitance region is seen.

REFERENCES

1. S. Motupally, C. C. Streinz and J. W. Weidner, *J. Electrochem. Soc.*, 1995, **142**, 1401.
2. V. Srinivasan and J. W. Weidner, *J. Electrochem. Soc.*, 1999, **146,** 1650.