Supporting Information

Water-in-Acid Gel Polymer Electrolyte Realized through a PhosphoricAcid-Enriched Polyelectrolyte Matrix toward Solid-State Supercapacitors

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Number of pages: 11 (Page **S2-S3**: Equations and calculations used for performance assessment)

Number of Figures: 11 (Page **S4-S8)**

Number of Tables: 2 (Page S9 and S10)

Equations and calculations used for performance assessment[1]

The swelling ratio (Q) is calculated from **Equation S1**

$$Q = \frac{Ws-Wd}{Wd} \times 100 \qquad \text{(S1)}$$

Ws = Mass of Swollen specimen
Wd = Mass of pre-swollen specimen

The equation (2) is used for the calculation of specific gravimetric (F g^{-1})/areal capacitance (mF cm^{-2}) from the charge-discharge method.

$$C = \frac{2\times(I\times\Delta t)}{\Delta V * M \text{ or } A} \qquad \text{(S2)}$$

where,

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

In order to get the single electrode capacitance, the obtained device capacitance was multiplied by a factor of 2 which is included in **Equation S2**.
Gravimetric energy density (E_d) and power density (P_d) were calculated from the capacitance value obtained from the charge-discharge method.

$$\text{Energy density } (E_d)\ ((\text{Wh kg}^{-1})) = \frac{Cs}{8\times3.6}\ V^2 \qquad \text{(S3)}$$

where,
'Cs' is the specific capacitance calculated by the charge-discharge (F g^{-1}) method and 'V' is the voltage window.

$$\text{Power density } (P_d)\ ((\text{W kg}^{-1})) = \frac{Ed}{t} \qquad \text{(S4)}$$

where, 'E_d' is the energy density from **Equation S3** and 't' is the discharge time in hour calculated from the discharge curve.

The ionic conductivity of the GPEs was calculated from **Equation S5** and S**6**.

$$\rho\ (\Omega\ \text{cm}) = \frac{RA}{l} \qquad \text{(S5)} \qquad\qquad \sigma\ (S\ cm^{-1}) = \frac{1}{\rho} \qquad \text{(S6)}$$

σ= Conductivity of the membrane

ρ = Resistivity of the membrane
R = bulk resistance of the membrane
A = Area of the membrane
l = Thickness of the membrane

The Arrhenius relationship is given in **Equation S7**.

$$\sigma = \sigma^{o} \exp(-E_a/RT) \qquad (S7)$$

In the above equation, σ, σ^{o}, Ea, R, and T are the ionic conductivity, the pre-exponential factor, the activation energy for ion transport, the gas constant and the absolute temperature, respectively.
The activation energy calculated for He-Ao-Ac-sw is obtained from the linear fitting of the ln σ *vs*. 1/T plot.

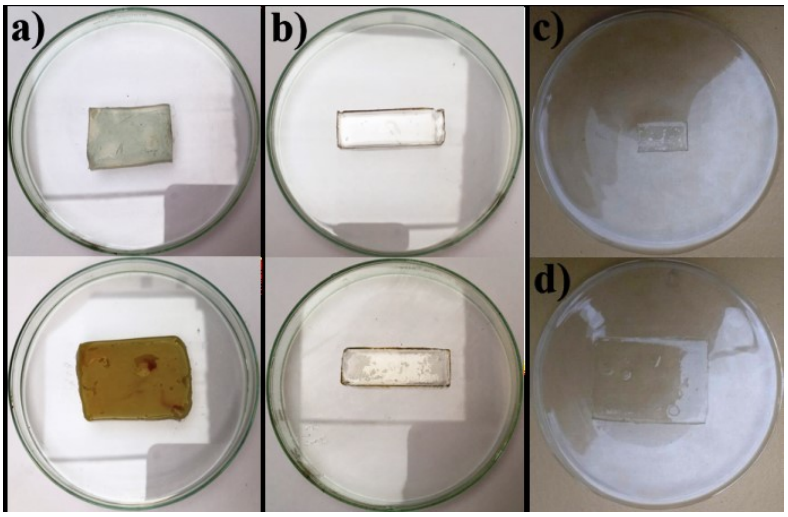

Figure S1. *The digital images of (a) PAOETMA gel and (b) PHEMA gel before and after swelling in H_3PO_4, (c) pre-swollen He-Ao-Ac-30% film and (d) swollen He-Ao-Ac-sw PGPE.*

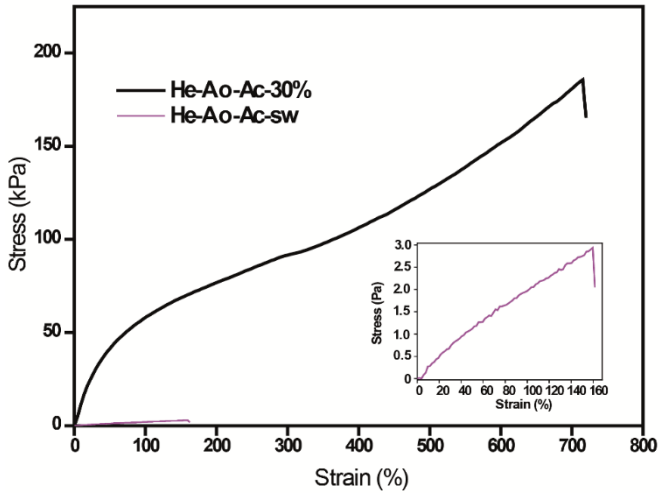

Figure S2. *The plot representing the tensile stress vs. strain for the He-Ao-Ac-30%. Similar plot corresponding to the He-Ao-Ac-sw PGPE specimen is given in the inset.*

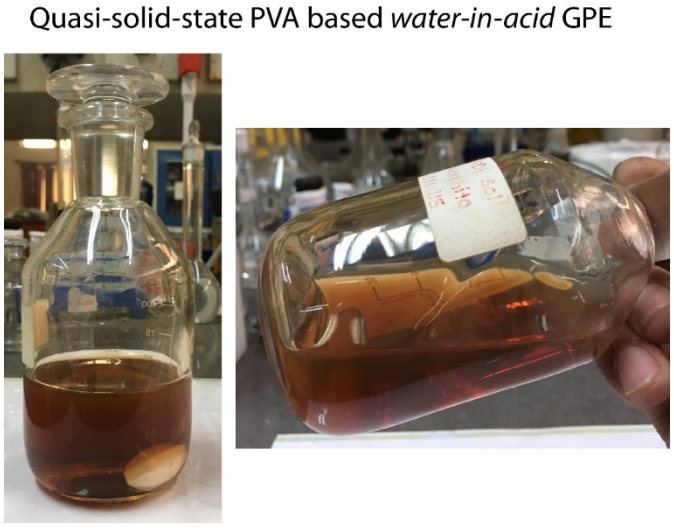

Figure S3*. Highly viscous nature of the PVA based water-in-acid GPE.*

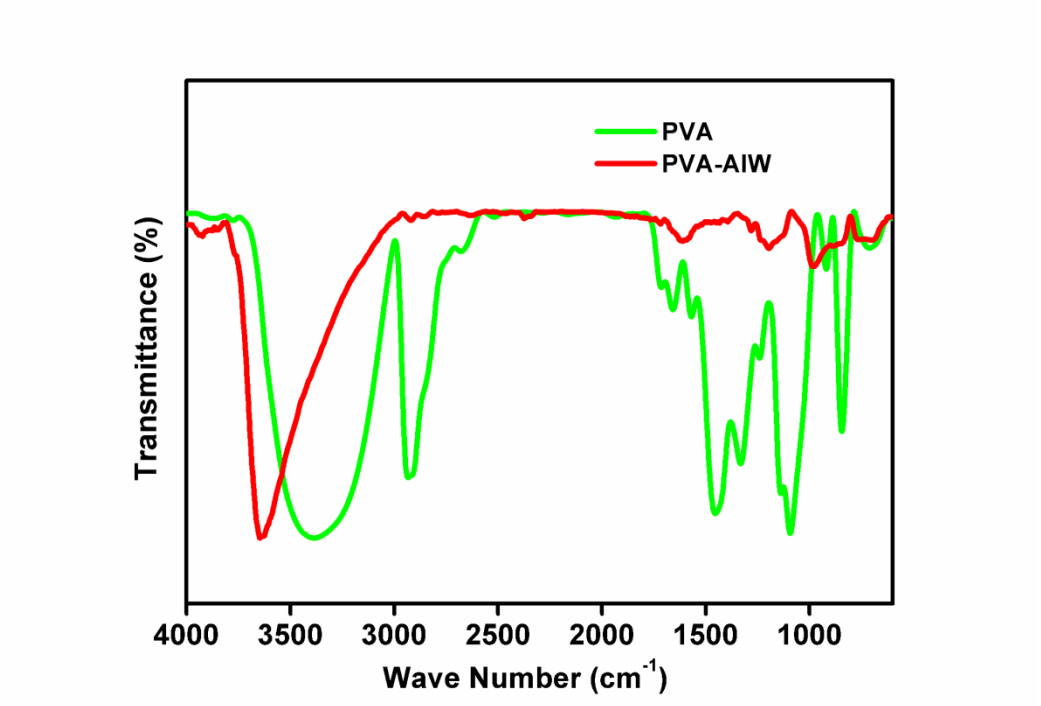

Figure S4. *FTIR spectra of the pristine PVA powder and the PVA-AIW GPE.*

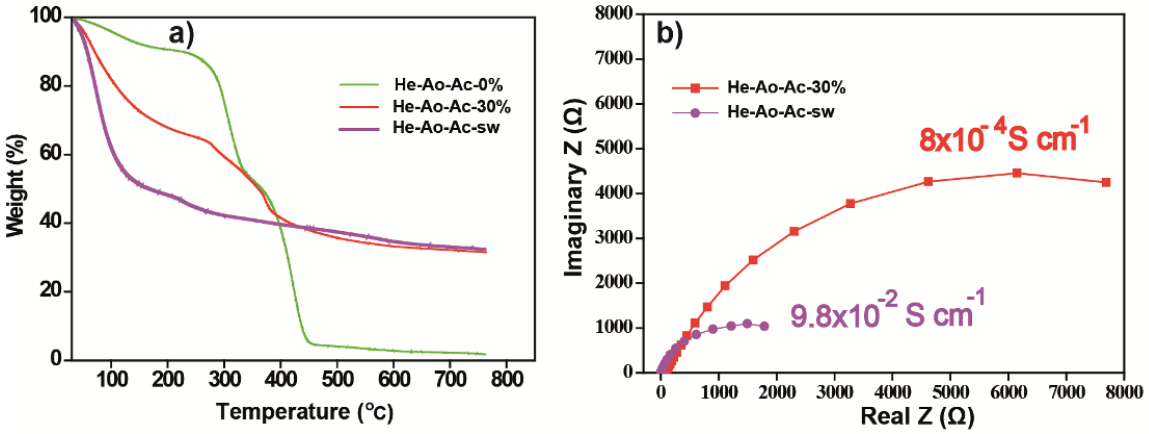

Figure S5. *(a) The thermogravimetric analysis (TGA) of the pre-swollen films (He-Ao-Ac-0% and 30%) and the water-in-acid PGPE (He-Ao-Ac-sw) and (b) The Nyquist plots corresponding to He-Ao-Ac-30% and He-Ao-Ac-sw PGPE over the whole frequency range.*

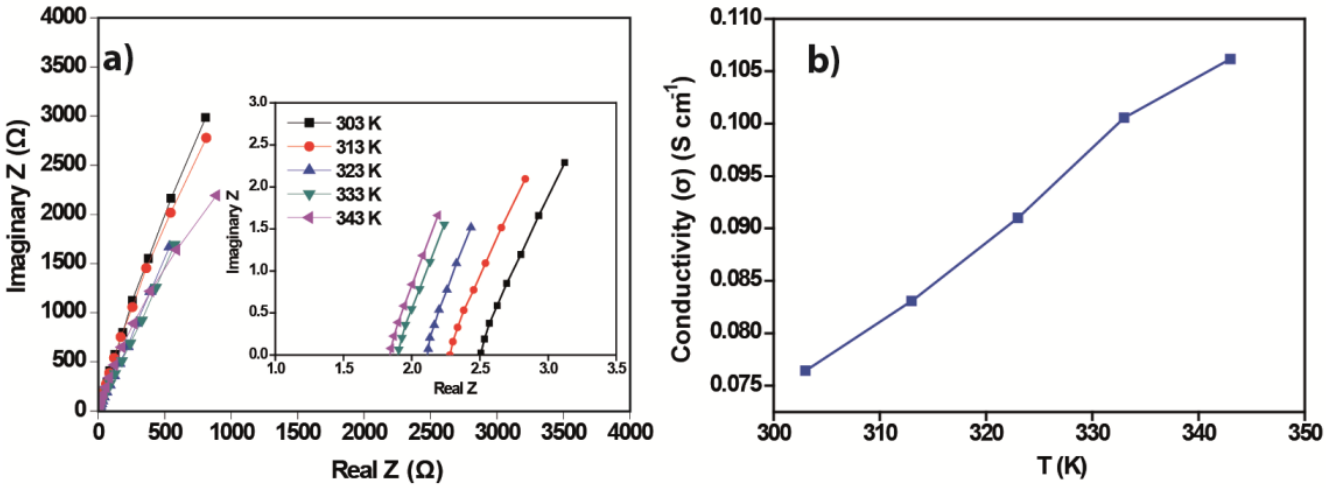

Figure S6. *(a) The Nyquist plots corresponding to the He-Ao-Ac-sw PGPE film at different temperatures ranging from 30 to 70°C; (b) the ionic conductivity values calculated from the ESR values obtained from the Nyquist plots given in Figure S6a.*

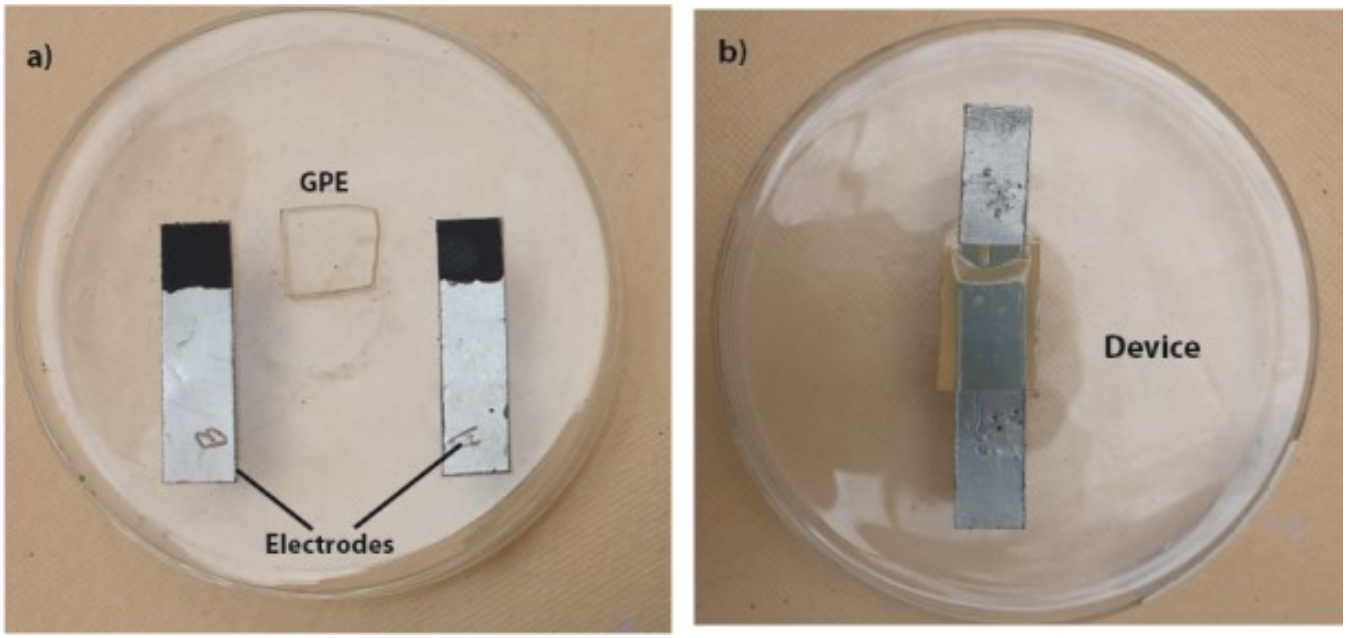

Figure S7. *(a) The digital images of the various components viz., electrodes and the water-in-acid PGPE used for the SC device fabrication; (b) digital image of the final device.*

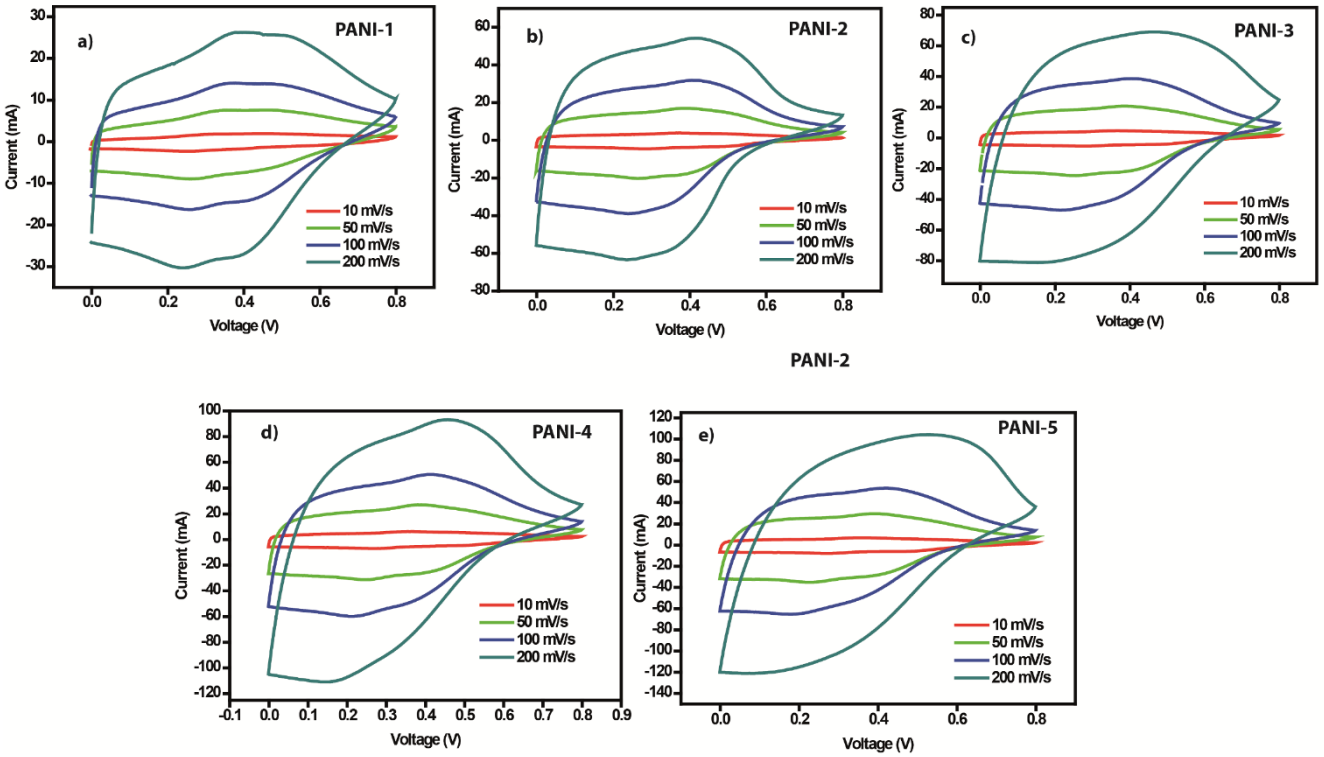

Figure S8. *(a) to (e) The full CV profiles for the devices (PANI-1 to 5) recorded at various scan rates from 10 mVs^{-1} to 200 mVs^{-1}.*

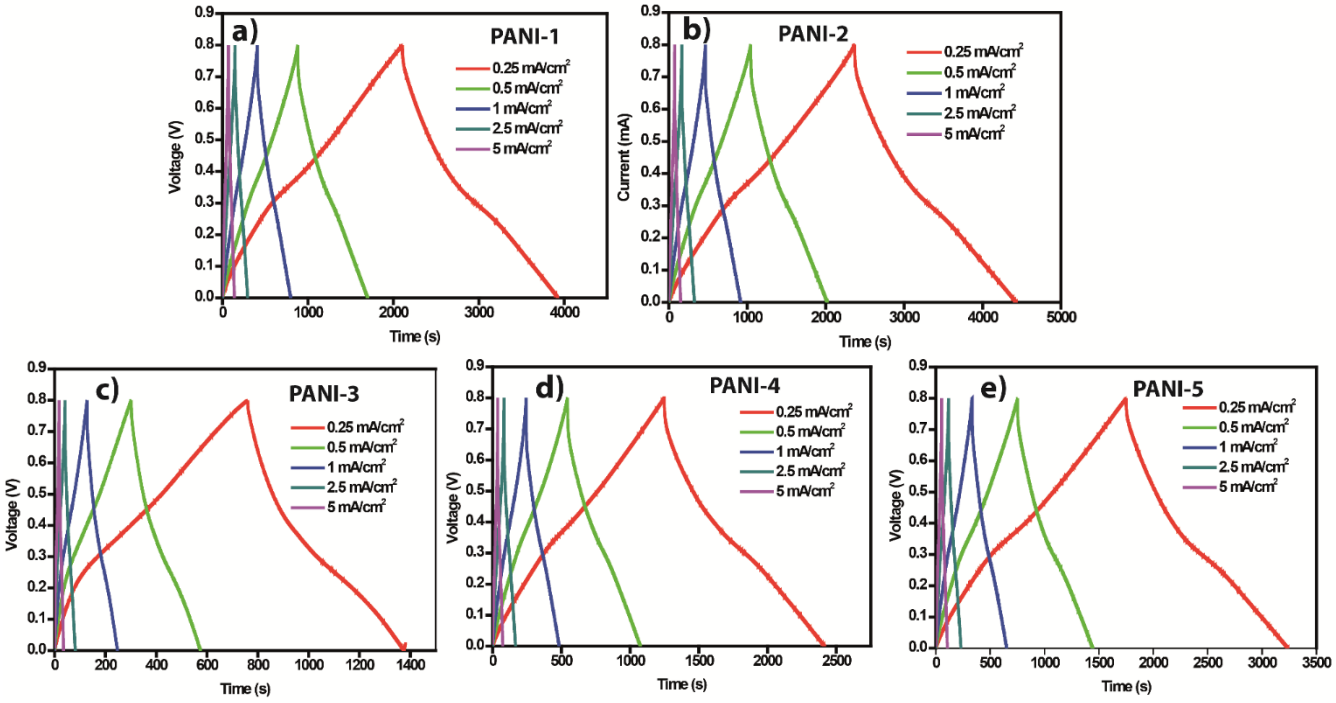

Figure S9. *(a) to (e) The CD profiles for the devices (PANI-1 to 5) recorded at various current densities from 0.25 to 5 mA cm^{-2}.*

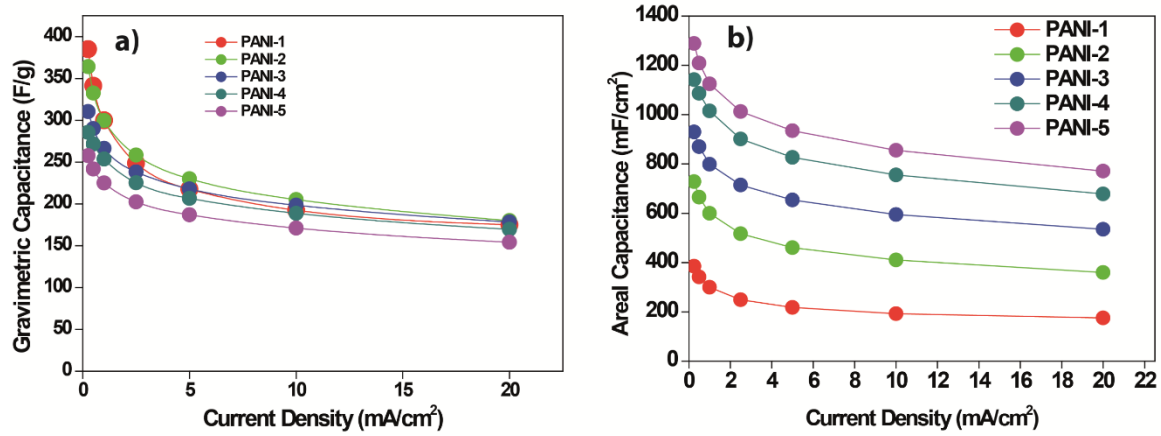

Figure S10. *(a) The plots representing the specific gravimetric capacitance corresponding to the PANI-x SC devices at various scan rates; (b) the plot representing the specific areal capacitance corresponding to the PANI-x SC devices at various current densities.*

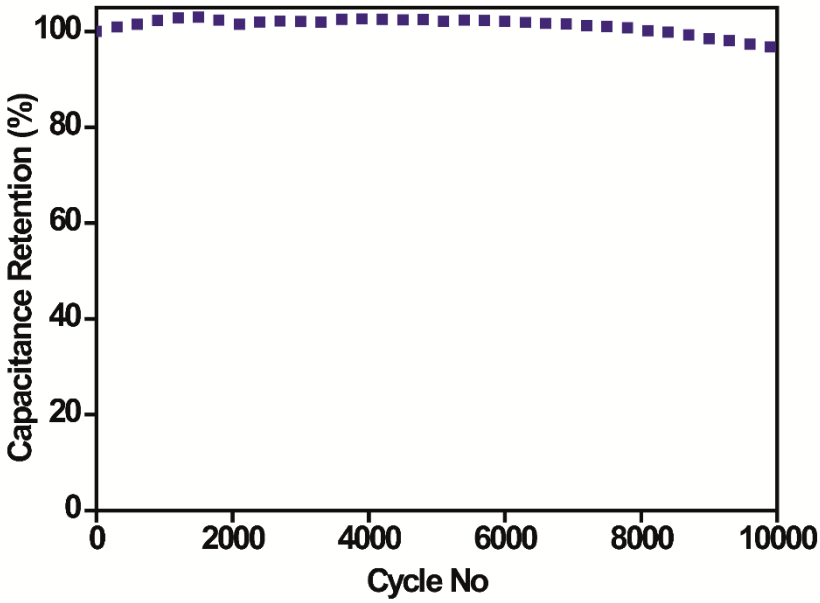

Figure S11. *Cycling stability of the PANI-5-PVA-WIA device at a current density of 10 mA* cm^{-2}.

Table S1: *The ionic conductivity of the proton conducting GPEs already reported in the literatures and the water-in-acid PGPE reported in this work are compared and summarised.*

Composition of the polymer electrolyte	**Physical nature of the polymer electrolyte**	**Ionic Conductivity**	**Experimental conditions**	**Reference in the main text**
PHEMA-PTMPA-H_3PO_4	*in-situ* prepared GPE film	2.80×10^{-2} S cm^{-1}	At 303 K	3
Carboxymethyl Cellulose doped with oleic acid and plasticized with glycerol (CMC-OA-Gly SBE)	free-standing film	1.64×10^{-4} S cm^{-1}	At 303 K	37
Gellan gum+Borax+H_3PO_4/H_2SO_4/HCl	free-standing film	5.1×10^{-3} to 3.7×10^{-4} S cm^{-1}	At 303 K	38
PVA-H_3PO_4	free-standing film	4.1×10^{-3} S cm^{-1}	At 303 K	39
PVA-H_3PO_4	free-standing film	2.56×10^{-3} S cm^{-1}	Room temperature	40
PVA-H_3PO_4	free-standing film	3.4×10^{-3} S cm^{-1}	At 303 K	41
PVP-NH_4Br	free-standing film	1.06×10^{-3} S cm^{-1}	At 303 K	42
PEO + 8 wt% HCF_3SO_3 + 50 wt% DMA + 3 wt% SiO_2	free-standing film	7.38×10^{-3} S cm^{-1}	At 303 K	43
PVdF-HFP+EMITf+ NH_4Tf	quasi-solid-state	2.3×10^{-2} S cm^{-1}	Room temperature	44
P(MMA-co-HEMA) (60 wt.% of HEMA) + (PC+DMF) (30 wt.% of DMF)+40 wt.% Diphenyl phosphate	quasi-solid-state	5.7×10^{-4} S cm^{-1}	At 283 K	5
PVA-Gluteraldheyde-$HClO_4$	free-standing film	*ca*. 1×10^{-3} S cm^{-1}	At 298 K	6
P(HEMA-co-AOETMA)+H_3PO_4	**free-standing film**	**9.8×10^{-2} S cm^{-1}**	**At 303 K**	**This work**

***Table S2**: A table summarising the electrochemical performance of the previously reported H_3PO_4 electrolyte-based PANI SCs (some other electrode/electrolyte based SCs are also mentioned) compared to the water-in-acid PGPE based SC reported in this work are compared and summarised.*

Electrolyte used	**Details of Device Fabrication**	**ESR**	**Specific Capacitance**	**Cyclic stability**	**Reference in main text**
PVA-H_3PO_4	Polypyrrole as electrode material and quasi-solid-state electrolyte. Active material loading is not mentioned.	9.9 to 16.5 Ω	84 to 93 F g^{-1} at 0.5 A g^{-1}	74 to 84 % capacitance retention after 2000 cycles at 0.5 A g^{-1}	41
PVA-H_3PO_4	Neat PANI as electrode material and quasi-solid-state device configuration. Active material loading is not mentioned.	> 1.5 Ω	293 F g^{-1} at 0.5 A g^{-1}	60 % retention after 1000 cycles at 1 Ag^{-1}	57
PVA-H_3PO_4	Screen printed MnO_2 based microsupercapacitor	-	-	80% capacitance retention after 1000 cycles at 50 μA cm^{-2}	58
PVA-H_3PO_4	Quasi-solid-state electrolyte along with PANI-MWCNT thin film	-	7.8 mF cm^{-2} at 0.5 mA current.	91 % retention of specific capacitance after 1000 cycles	59
PVA-H_3PO_4	MnO_2/PANI coaxial nanowires, quasi-solid-state electrolyte, electrode mass loading of 8.5 mg cm^{-2} loading	2.9 Ω	346 mF cm^{-2} at 5 mV s^{-1}	Almost 100% retention after 1000 cycles at 1.5 mA cm^{-2} current density	60
PVA-H_2SO_4	cellulose nanofibers-PANI electrode, quasi-solid-state electrolyte	*ca*. 1.9 Ω	406.8 F g^{-1} at 1 A g^{-1}	80% capacitance retention after 1000 cycles	61
P(HEMA-co-AOETMA)+H_3PO_4	**PANI electrodes sandwiched in between the *water-in-acid* PGPE. PANI mass loading from 1 to 5 mg cm^{-2}**	**0.61 to 0.78 Ω**	**385 F g^{-1} at a current density of 0.25 mA cm^{-2}/0.25 A g^{-1} for PANI-1 mg cm^{-2} and 285 F g^{-1}/1288 mF cm^{-2} at 0.25 mA cm^{-2} for PANI-5 mg cm^{-2}**	**100% capacitance retention after 9000 continuous charge discharge cycles at 10 mA cm^{-2}.**	**This work**

1. Vijayakumar, V.; Anothumakkool, B.; Torris A. T, A.; Nair, S. B.; Badiger, M. V.; Kurungot, S., An all-solid-state-supercapacitor possessing a non-aqueous gel polymer electrolyte prepared using a UV-assisted in situ polymerization strategy. Journal of Materials Chemistry A 2017, 5 (18), 8461-8476.