

## Support Information: A Metal-free All-organic Ammonium-ion Battery with Low-temperature Applications

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### 1. Experimental Section

#### 1.1 Synthesis of Polypyrrole

0.86 g Sodium Dodecyl Sulphate (SDS) as a surfactant was added to 30 ml de-ionized water, followed by vigorous stirring for 30 mins to obtain a clear solution. 3 ml pyrrole monomer was then added dropwise. Afterwards, FeCl<sub>3</sub> solution of the required molarity was added dropwise and allowed to polymerize for 3 hours at room temperature. A black solution was formed, indicating successful polymerization. It was washed and filtered several times with de-ionized water. The polymer powder was dried in a vacuum oven at 60°C for 24 hours.

#### 1.2 Synthesis of Polyaniline.

PANI was synthesized by a chemical oxidation method. Typically, 0.365 mL aniline and 15 mL 1 M HCl were added in a beaker under stirring in an ice bath to maintain a low temperature range of 0 – 5 °C. After 1 h of continuous stirring, 5 mL of 1 M HCl with dissolved 0.228 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (APS) as an oxidant was added into the mixture dropwise whilst under continuous stirring in the ice bath. After a few minutes, the colorless solution turned dark green, showing polymerization had occurred. After the reaction continued for 1 h, the solution was taken out and washed with deionized water, and PANI precipitates were collected then put in an oven for drying at 60°C for 12 h.

#### 1.3 Material Characterization.

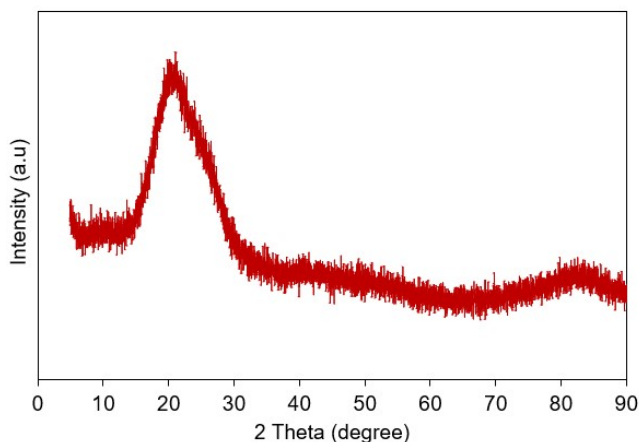
X-Ray diffraction measurements were collected at rate of 2° min<sup>-1</sup> using Rigaku MiniFlex XRD with Cu K $\alpha$  radiation with wavelength 1.54Å. Scanning electron imaging and EDS mapping was done using FEI Quanta 3D FEG field emission scanning electron microscope. Raman data was collected using the Reinshaw in Via Reflex Raman Microscope and X-ray photoelectron spectroscopy (XPS) measurements were done using AXIS165 spectrometer. Bruker Avance Neo 700 MHz spectrometer was used for NMR characterization for the electrolyte in deuterium solvent.

#### 1.3 Electrochemical Measurement

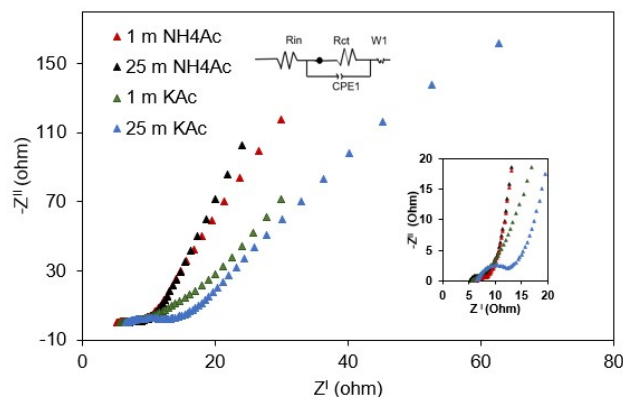
For the three-electrode cell measurements, the electrode was prepared by mixing the as-prepared PPy, carbon black and polyvinylidene fluoride (PVDF) binder at a weight ratio of 7:2:1 in dimethylformamide. The slurry was then cast onto the carbon fiber paper and dried at 60°C in

an oven. The mass loading of the electrode is about 3 mg/cm<sup>2</sup>. The electrochemical performance was tested in an three-electrode cell, in which the PPy electrode, graphite rod, and saturated Ag/AgCl, serve as the working electrode, counter electrode, and reference electrode, respectively. The electrolyte is 200 ml of 1 m or 25 m aqueous solution of NH<sub>4</sub>Ac or KAc. Cyclic voltammetry (CV) measurements and galvanostatic charge- discharge (GCD) tests were conducted on an electrochemical work station CHI 6504C (CH Instruments, Inc. Austin, TX) over a potential range of 0.5 – -1 V. Electrochemical impedance spectroscopy (EIS) measurements were operated by applying an AC potential of 5 mV amplitude in a frequency range from 0.01 to 100 kHz.

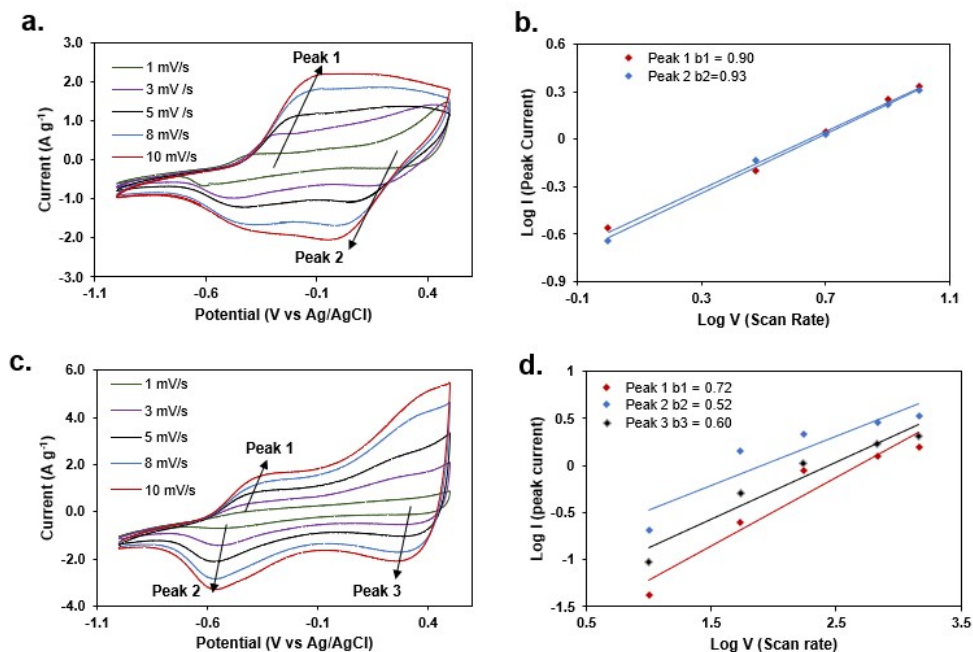
For the full PANI/PPy full aqueous batteries, a 2032 coin-type cell was assembled using PANI anode and PPy cathode coupled with the electrolyte (NH<sub>4</sub>Ac or KAc) and separator. The working electrodes, i.e., PANI and PPy, were fabricated by rolling 60 wt% active material, 30 wt% conductive carbon (Super P), and 10 wt% polytetrafluoroethylene (PTFE) into thin film. Galvanostatic charge-discharge experiments were carried out on an eight-channel battery analyzer (MTI corporation) with a voltage range of 0 - 1 V. Cyclic voltammetry measurements and electrochemical impedance spectroscopy was conducted on an electrochemical workstation (CHI 6504C) with a frequency range of 100 kHz to 0.01 Hz.



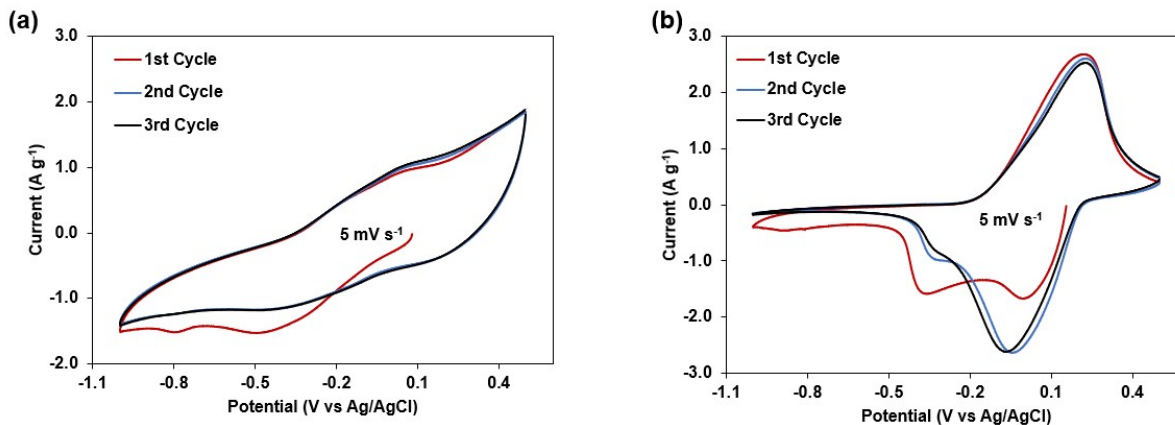
**Figure S1:** XRD spectrum of PPy.



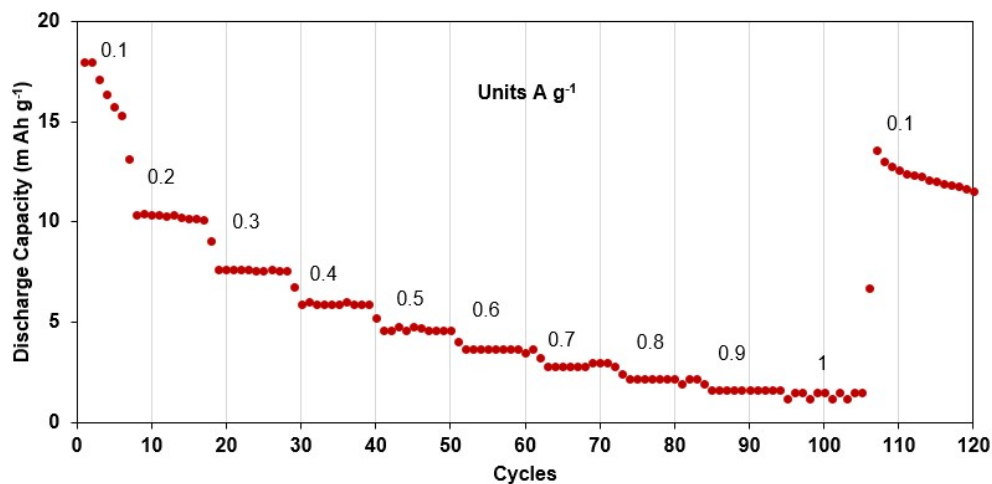
**Figure S2:** Electronic Impedance Spectroscopy spectra of the PPY electrode in 1 m NH<sub>4</sub>Ac, 25 m NH<sub>4</sub>Ac, 1 m KAc, and 25 m KAc electrolytes.



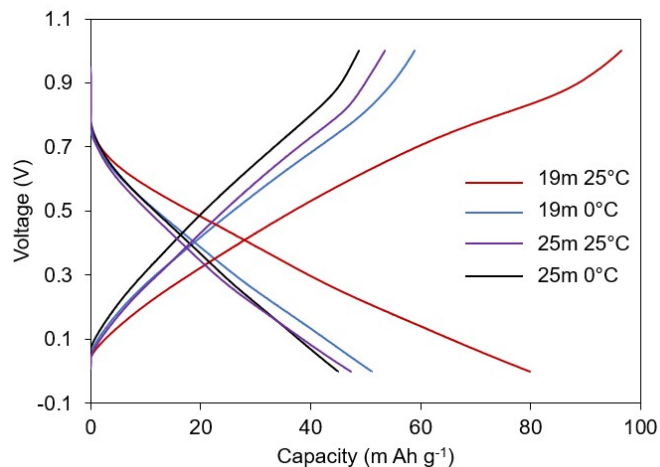
**Figure S3:** The CV profiles of PPY in 1 m NH<sub>4</sub>Ac at various scan rates; (b) Log *i* (current) versus Log *v* (scan rate) at specific reduction/oxidation states based on the CV data in (a); (c) CV profiles of PPY in 1 m KAc at various scan rates; (d) Log *i* (current) versus Log *v* (scan rate) at specific reduction/oxidation states based on the CV data in (c).



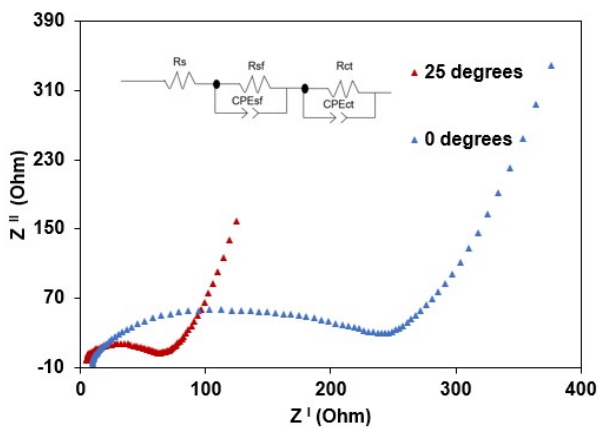
**Figure S4:** Cyclic voltammograms of (a) PPy and (b) PANI in the three-electrode set-up with 25 m NH<sub>4</sub>Ac electrolyte at a scan rate of 5 mV s<sup>-1</sup> at 0 °C.



**Figure S5:** Rate performance of the full PANI/PPy cell with the 19 m KAc electrolyte.



**Figure S6:** Initial charge/discharge curves of PANI/PPy battery cells with 19 m and 25 m NH<sub>4</sub>Ac electrolytes at 0 and 25°C, respectively, when cycled at 0.1 A g<sup>-1</sup>.



**Figure S7:** Electronic impedance spectroscopy spectra of the full PPy/PANI cell with the 19 m NH<sub>4</sub>Ac electrolyte at 25°C and 0°C.

