

A full metal-free flexible Ammonium-ion battery with biodegradable hydrogel electrolyte

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1. Experimental section

1.1 Materials synthesis

In a beaker, 0.35 ml of 99% aniline monomer (Alfa Aesar) was mixed with 15 ml of 1 M HCl. The resulting mixture was stirred in an ice water bath (0°C) for one hour. Subsequently, a solution containing 5 ml of 1 M HCl and 0.228 g ammonium persulfate was added dropwise to the mixture. Within minutes, the initially colorless solution transformed into a green hue. The mixture underwent additional stirring in the ice water bath for an additional hour. The resulting solution was then washed 2-3 times with DI H₂O using a centrifuge (each time for 3 minutes at 4400 RPM) and subsequently dried at 60°C for 5 hours. The resulting dried substance was finely ground into powders.

The synthesis of polypyrrole (PPy) involved mixing 0.86 g sodium dodecyl sulfate with 30 ml DI H₂O under continuous stirring. After 30 - 40 minutes, a clear solution was achieved. Following this, 3 ml pyrrole monomer was added, and 7.2 ml of 2.5 M FeCl₃ was added dropwise (maintaining a PPy to FeCl₃ ratio of 1:2.4). The solution was then allowed to polymerize under stirring at 25°C for 3 hours, resulting in a black solution indicative of complete polymerization. The solution underwent washing 5 - 6 times with DI H₂O and was subsequently dried in an oven at around 60°C for 24 hours.

For the electrode material, 30 mg active material (cathode or anode) was measured and combined with 15 mg carbon black in a mixing bowl. A few drops of ethanol were added, and the mixture was manually ground until dry. This process was repeated 3 - 4 times. Subsequently, 5 mg binder was added to the dried substance with a few drops of ethanol. The mixture was stirred until the ethanol evaporated, and the remaining material was scraped. The film roller thickness was set to 0.12 mm, and the process was repeated 3 - 4 times. The thickness was adjusted to 0.08 mm, and the film was rolled until a smooth, narrow film was obtained. The film was carefully removed, placed on a measuring paper, sprayed with ethanol, covered with another measuring paper, and cut vertically through the middle and then horizontally ten times. The resulting film pieces were placed in a petri dish and dried in an oven at 60°C for 10 minutes to evaporate ethanol.

The hydrogel electrolyte was obtained by dissolving 1 g xanthan gum powders in 2 ml deionized water, ensuring a homogeneous mixture at room temperature overnight. Subsequently, 1 m (or 2 m or 3 m) solution of (NH₄)₂SO₄ (VWR Chemicals ≥99.0%) in 3 ml deionized water was introduced into the mixture. The resulting mixture was stirred for 3 - 4 days to produce the 1 m, 2 m, and 3 m QSS electrolytes, respectively. Hydrogel electrolytes with varied gum contents were synthesized following the procedure similar to above but using 0.5 g xanthan gum and 2 g xanthan gum in 2 ml DI water, respectively.

1.2 Materials characterization

Electron microscopy imaging and EDS mapping of the samples were performed using a FEI Quanta 3D FEG field emission scanning electron microscope. X-ray diffraction (XRD) measurements were taken using a Rigaku MiniFlex XRD with a 1.54 \AA wavelength at a rate of 2° min^{-1} . The Reinshaw in Via Reflex Raman microscope was used to acquire Raman data, while the AXIS165 spectrometer was used to obtain X-ray photoelectron spectroscopy (XPS) data.

1.3 Battery cell fabrication and testing

Coin cells of the 2032 types were constructed, incorporating PANI anode, PPy cathode, and aqueous or hydrogel electrolyte, along with a polymer separator. Throughout this experiment, the mass ratio of anode and cathode was maintained in the ratio of 1:2 and the electrolyte volume remained consistent in each coin cell. To introduce the electrolyte, a syringe was utilized to add it drop by drop between each layer of the coin cell. The sealed coin cells were achieved using a crimping machine from MTI Corporation. The flexible battery was fabricated by sandwiching a hydrogel electrolyte between the PANI anode and PPy cathode, utilizing stainless steel foils as current collectors for efficient electron flow and copper tapes as conducting leads, sealed by plastic films for structural integrity. Galvanostatic charge-discharge curves within the voltage range of 0 to 1 V were acquired using battery analyzers also provided by MTI Corporation. Cyclic voltammetry and electrochemical impedance spectroscopy were recorded using an electrochemical workstation (CHI 6504C) spanning the frequency range of 100 kHz to 0.01 Hz.

2. Supplementary results and discussion

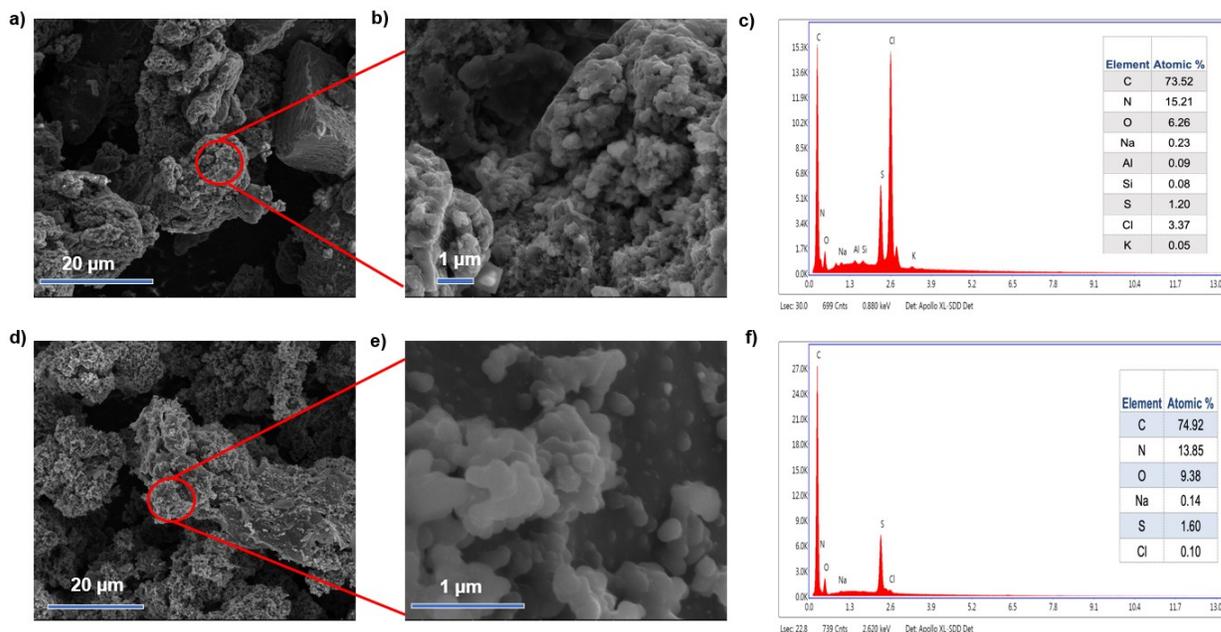


Figure S1. Characterizations of PANI powders: (a) SEM image, (b) magnified view, (c) EDS spectrum. Characterizations of PPy powders: (d) SEM image, (e) magnified view, (f) EDS spectrum.

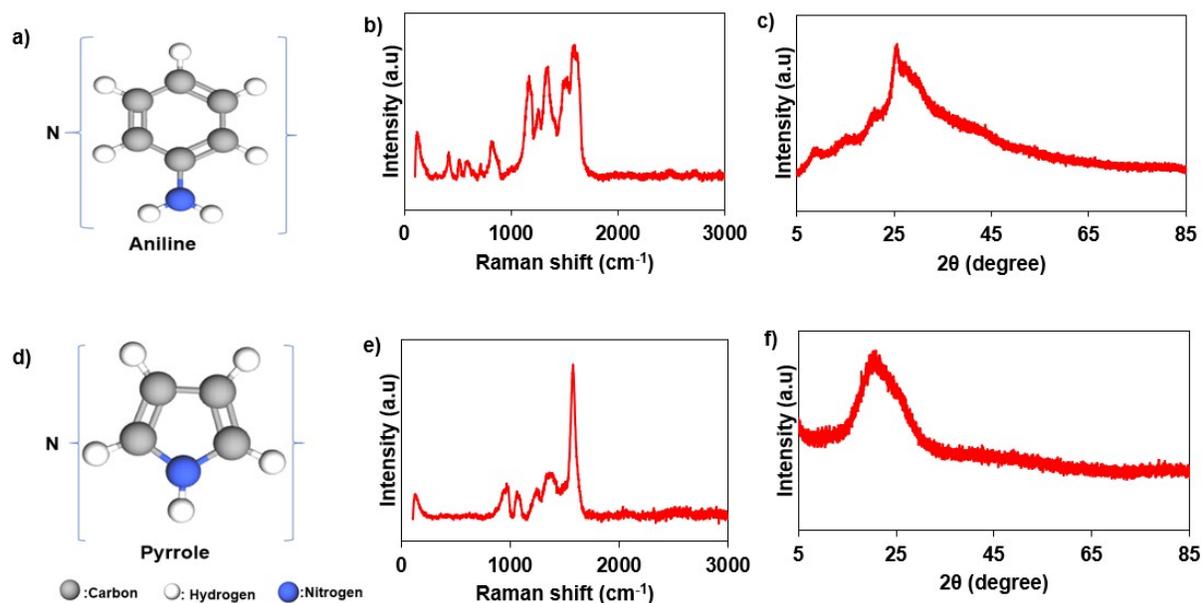


Figure S2. PANI powders: (a) molecular structure with N numbers of molecules, (b) Raman spectrum, (c) XRD pattern. PPy powders: (d) molecular structure with N numbers of molecules, (e) Raman spectrum, (f) XRD pattern.

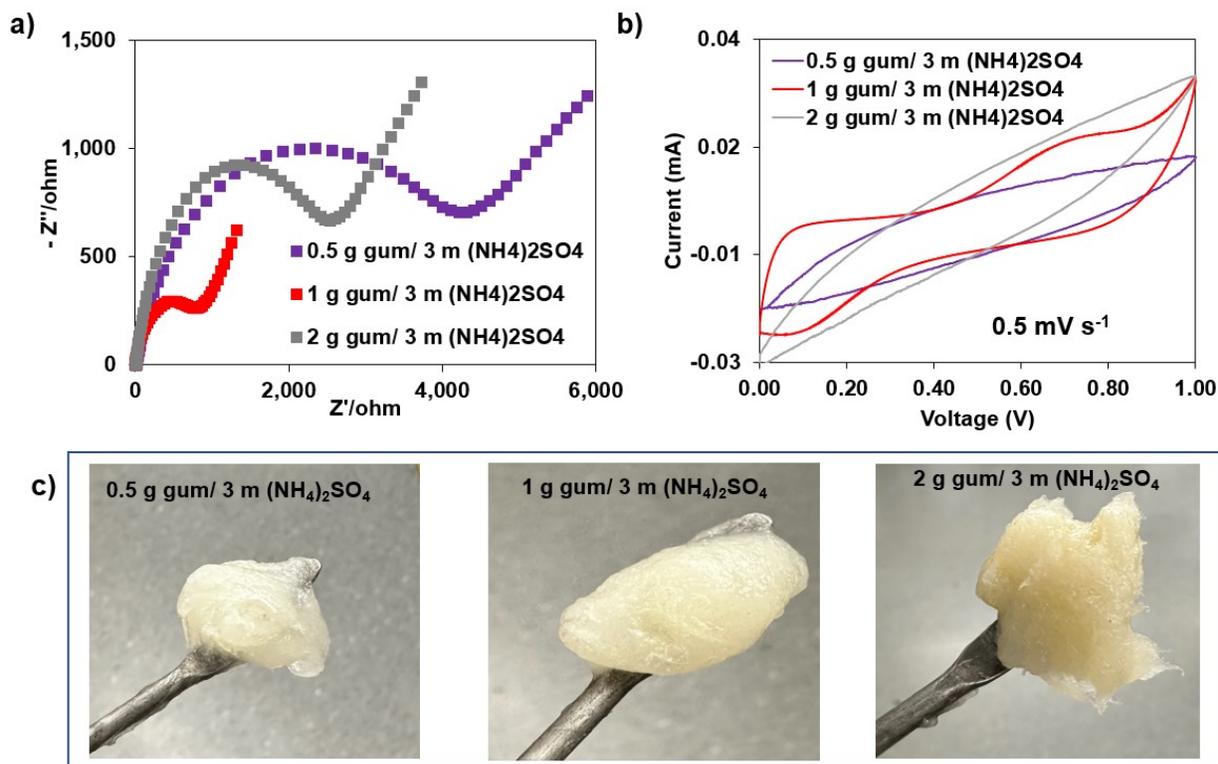


Figure S3. Characterizations of the three hydrogel electrolytes prepared using 0.5 g, 1 g, 2 g gum, respectively: (a) Impedance spectra of the electrolytes, (b) CV curves of the PANI/PPy batteries based on the three electrolytes at 0.5 mV s^{-1} , (c) photos of the three electrolytes.