

## Supporting Online Material

### For *Ultrafast All-Polymer Paper-Based Batteries*

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## Materials and Methods

*Chemicals and reagents:* Cladophora green algae were collected from the Baltic Sea. Five hundred grams of Cladophora green algae was bleached with 180 g of NaClO<sub>2</sub> in 0.5 liter acetic buffer. The mixture was diluted to 5 liters, poured into a plastic bag and stored in a water-bath for 3 h at 60 °C. The product was washed until neutrality (pH ~7) as indicated by coloration of a paper indicator (Universalindikator, Merck, Sweden) and filtered. Three liters of 0.5 M NaOH was added to the remainder, and the resultant product was stored at 60 °C in a water-bath overnight. The resultant pulp was washed till neutrality, filtered, and dried at room temperature. Dry, purified algae were ground prior to acidic hydrolysis (Fitz Mill type D6, Manesty Machines, UK). To 50 g of the product 1 liter of 5% HCl was added, and the suspension was heated till boiling. Once boiling, it was removed from the heat, and the slurry was allowed to stand overnight. The remainder was washed till neutrality, filtered and spray-dried (Minor Type 53, Niro Atomizer A.S., Denmark) at  $T_{in} = 205\text{--}210$  °C and  $T_{out} = 95\text{--}100$  °C with a feed-rate of 1.7 l/h. Pyrrole, iron (III) chloride, sodium chloride, Tween-80 and hydrochloric acid were used as supplied by VWR, Sweden.

*Preparation of composite:* A 300 mg sample of Cladophora powder was dispersed in 50 ml of water using high energy-ultrasonic treatment (VibraCell 750W, Sonics, USA) for 8 min and the dispersion was collected on a filter paper. Three ml of Py and one drop of Tween-80 was put in a volumetric flask and the total volume was brought to 100 ml. The collected cellulose cake was mixed with Py solution and dispersed using the ultrasonicator for 1 min. The dispersion was allowed to stand for 30 min and then collected on filter paper. Then 8 g of FeCl<sub>3</sub> was dissolved in 100 g of distilled water and run through the filter cake to induce the polymerization (the reaction was allowed to continue for 10 min prior to filtration). A fluffy sponge like cake was formed. Then, 100 mL of 0.1 M HCl was run through the cake. The product was then thoroughly washed with distilled water and dried (the cake was redispersed using an ultrasonicator to form a homogeneous layer). All of the steps above were performed at room temperature.

*Scanning electron microscopy (SEM):* Micrographs were taken with an environmental SEM (FEI/Philips XL 30, the Netherlands) in the high vacuum mode ( $3.5 \times 10^{-6}$  mbar). The samples were mounted on aluminum stubs using double-sided adhesive tape. Prior to imaging Au/Pt was sputtered on the samples to minimize charging.

*Transmission electron microscopy (TEM):* TEM images were recorded using a JEOL-3010 microscope, operating at 300 kV (Cs 0.6 mm, resolution 1.7 Å) with a CCD camera (Keen View, SIS analysis, size 1024 x 1024, pixel size 23.5 x 23.5 μm) at 150 000x magnification using low-dose conditions. As-prepared samples were crushed using a mortar and transferred to a holey-carbon TEM grid using ethanol.

*Surface area and pore volume:* N<sub>2</sub> gas adsorption and desorption isotherms were recorded with an ASAP 2020 (Micromeritics, USA). The specific surface area was obtained according to the BET method. The total pore volume of the samples was measured as the single point adsorption volume of pores with a diameter less than ~133 nm at a relative pressure of ~0.99.

*Thermogravimetric analysis:* Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA851 instrument. The cellulose/PPy composite sample was placed in an inert ceramic crucible and heated from 25 to 600 °C at a heating rate of 10 °C/min under the flow of air at 20 ml/min. The

weight of the Cladophora cellulose/PPy composite was 13 mg, whereas that of the reference Cladophora cellulose sample was 17 mg.

*Conductivity measurements:* The resistance of the sample was measured at room temperature using a semiconductor device analyzer (B1500A, Agilent Technologies USA). The voltage  $U$ , which was scanned between -1 and +1 V, was applied with titanium needle probes and the resulting dc current  $I$  was measured. Prior to the measurements, silver paint was pasted at the ends of rectangular samples to ensure good contact with the needle probes. The conductivity  $\sigma$  was then calculated as:  $\sigma = \frac{\Delta I}{\Delta U} \frac{L}{wd}$ , where  $\frac{\Delta I}{\Delta U}$  denotes the conductance of the sample obtained as the slope of the linear part of the current versus voltage curve,  $L$  is the length,  $w$  is the width and  $d$  is the thickness of the samples.

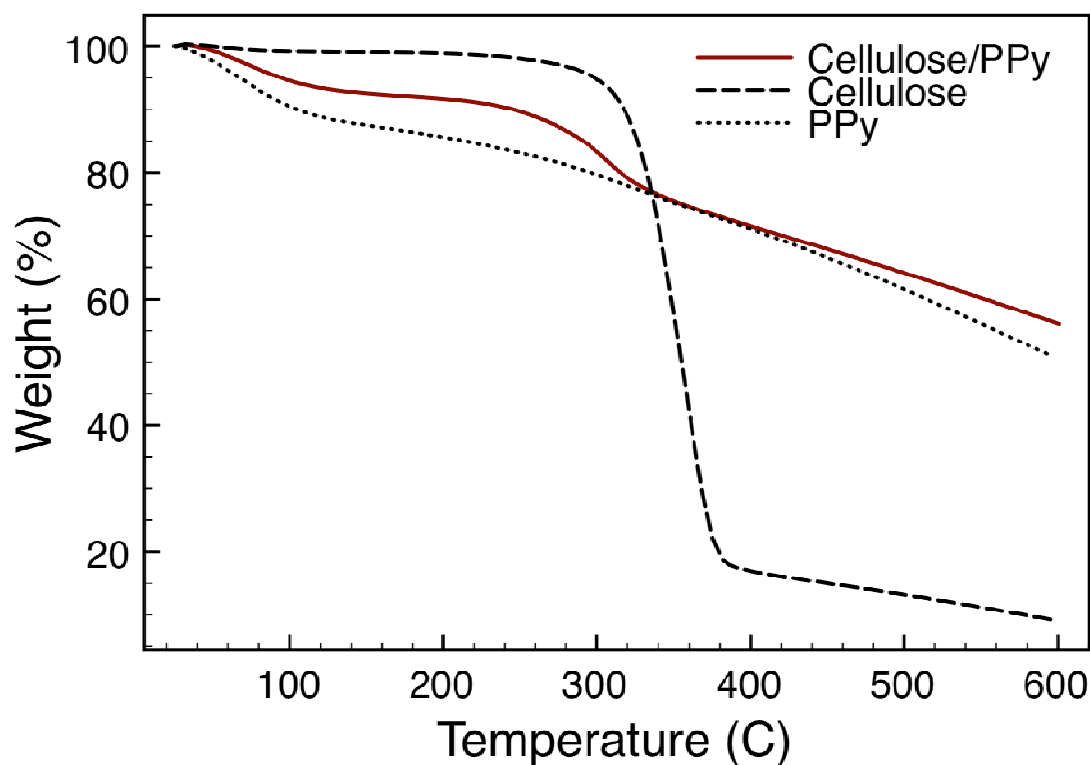
*Cyclic voltammetry:* Cyclic voltammetric measurements were performed in a standard three-electrode electrochemical cell utilizing an Autolab/GPES interface (ECO Chemie, The Netherlands) with the sample as the working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. The measurements were carried out in 2.0 M solutions of sodium chloride. The cyclic voltammograms were recorded at the applied potential from -0.9V to +0.9V in a new portion of the electrolyte. Scan rates used for measurements were varied between 3 and 20 mV/s. The typical dimensions of the samples used for cyclic voltammetry were 0.6 cm x 0.25 cm x (0.06-0.08 cm), which corresponded to sample weight of ~2.5 mg.

*Galvanostatic charge-discharge measurements:* Galvanostatic charge-discharge measurements were performed in 2.0 M sodium chloride solution using an Autolab/GPES interface (Eco Chemie, The Netherlands) in a two-electrode setup. A battery cell was constructed by using two identical pieces of the composite paper as cathode and anode separated by a sheet of filter paper (Whatman International Ltd, England) soaked with the electrolyte. Platinum foils were used as current collectors and the cell was sealed in polymer-coated aluminum pouches.<sup>S1</sup> In the experiments, the battery cell was charged and discharged by applying a constant current between 10 mA and 320 mA. The charging-discharging was cut off just below the limit of overoxidation of the polymer. This limit was evaluated experimentally by overoxidating a fresh sample for every used charging current. This data was then evaluated and the onset of overoxidation was determined by detecting the voltage at which the slope of the charging curve changes by investigating the derivative of the charging curve.

To test the long-term cycling stability of the battery cell, the charge-discharge measurements were continuously repeated for 100 cycles using  $\pm 320$  mA current, corresponding to a current density of 600 mA cm<sup>-2</sup>. The charge capacity was calculated from the charge curves of the measurements by multiplying charge current with charge time and normalizing by the total weight of the conductive paper composite material. The typical dimensions of the samples used for galvanostatic measurements were 1.0 cm x 0.5 cm x 0.1 cm, which corresponded to sample weight for each electrode of ~18.75 mg.

## Results

In **Figure S1** thermogravimetric (TGA) curves of the Cladophora cellulose/PPy composite material, pure Cladophora cellulose and of pure PPy are shown.

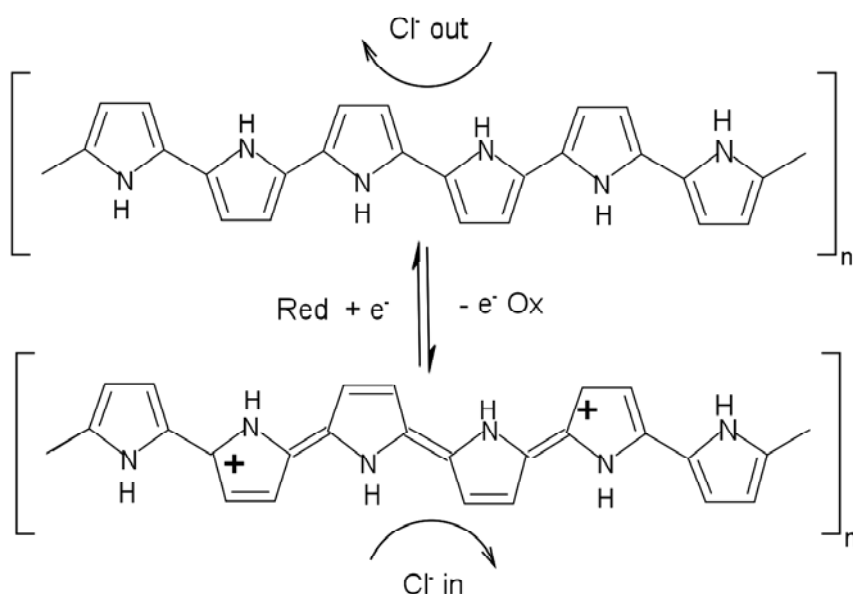


**Figure S1.** Thermogravimetric (TGA) curves of the Cladophora cellulose/PPy composite material, pure Cladophora cellulose and of pure PPy.

The reference Cladophora cellulose undergoes a rapid decomposition in a narrow range of temperatures between 300 °C and 360 °C with the formation of various anhydromonosaccharides including (1,6-anhydro- $\beta$ -D-glucopyranose), 1,6-anhydro- $\beta$ -D-glucofuranose, and other volatiles.<sup>S2,S3</sup> Nearly 85 wt % of Cladophora cellulose was decomposed at 400 °C and nearly 91 wt % was decomposed at 600 °C. The weight loss due to moisture evaporation at temperatures up to 100 °C in the Cladophora cellulose sample was less than 1 %, which is in good agreement with the previously reported data that Cladophora cellulose is non-hygroscopic at ambient relative humidities.<sup>S4,S5</sup> On the other hand, in the Cladophora cellulose/PPy composite, weight reduction due to water evaporation for temperatures up to 100 °C amounted to loss of about 5 wt %. It has been reported earlier that at temperatures around 200 °C PPy starts to rapidly decompose.<sup>S6,S7</sup> By considering the extent of cellulose decomposition at 400 °C, it can be concluded that roughly 2/3 of the composite consists of PPy which is in good agreement with TEM images and true density values. This value was also confirmed by a CHN analysis showing that the actual PPy content of an oxidized sample (containing Cl<sup>-</sup> counter ions) was 72 $\pm$ 3 wt%. The latter uncertainty refers to a 95% confidence interval based on 6 determinations assuming a fully oxidized PPy film containing 1 Cl<sup>-</sup> / 3 pyrrole units. Translated to a reduced sample, from which the Cl<sup>-</sup> ions have been expelled, the results of the CHN analysis gives a PPy content (without Cl<sup>-</sup> counter ions) of ~ 60%. Thus, in a battery, composed of both the reduced and the oxidized sample, the overall PPy content can be estimated to ~ 66%, in very close agreement with the TGA results.

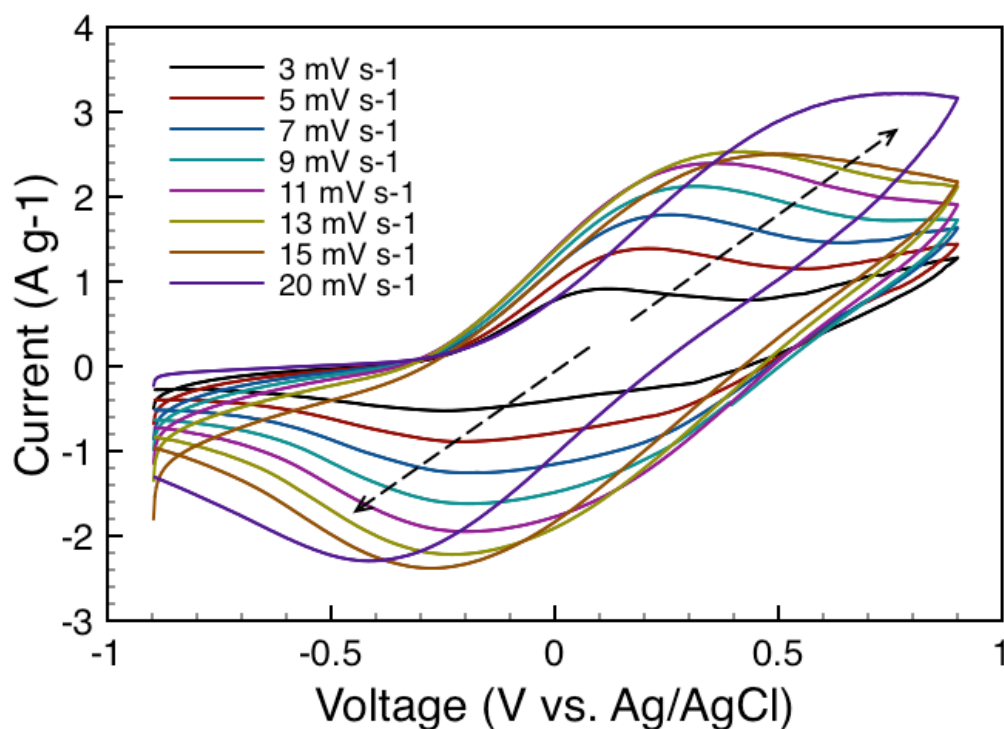
The close resemblance between the PPy and the composite TGA curves show that the cellulose fibers indeed are well covered by PPy which acts as a protective layer in the TGA experiments.

In **Figure S2** the charge and anion transfer during a red-ox process in composite paper electrode material is depicted.



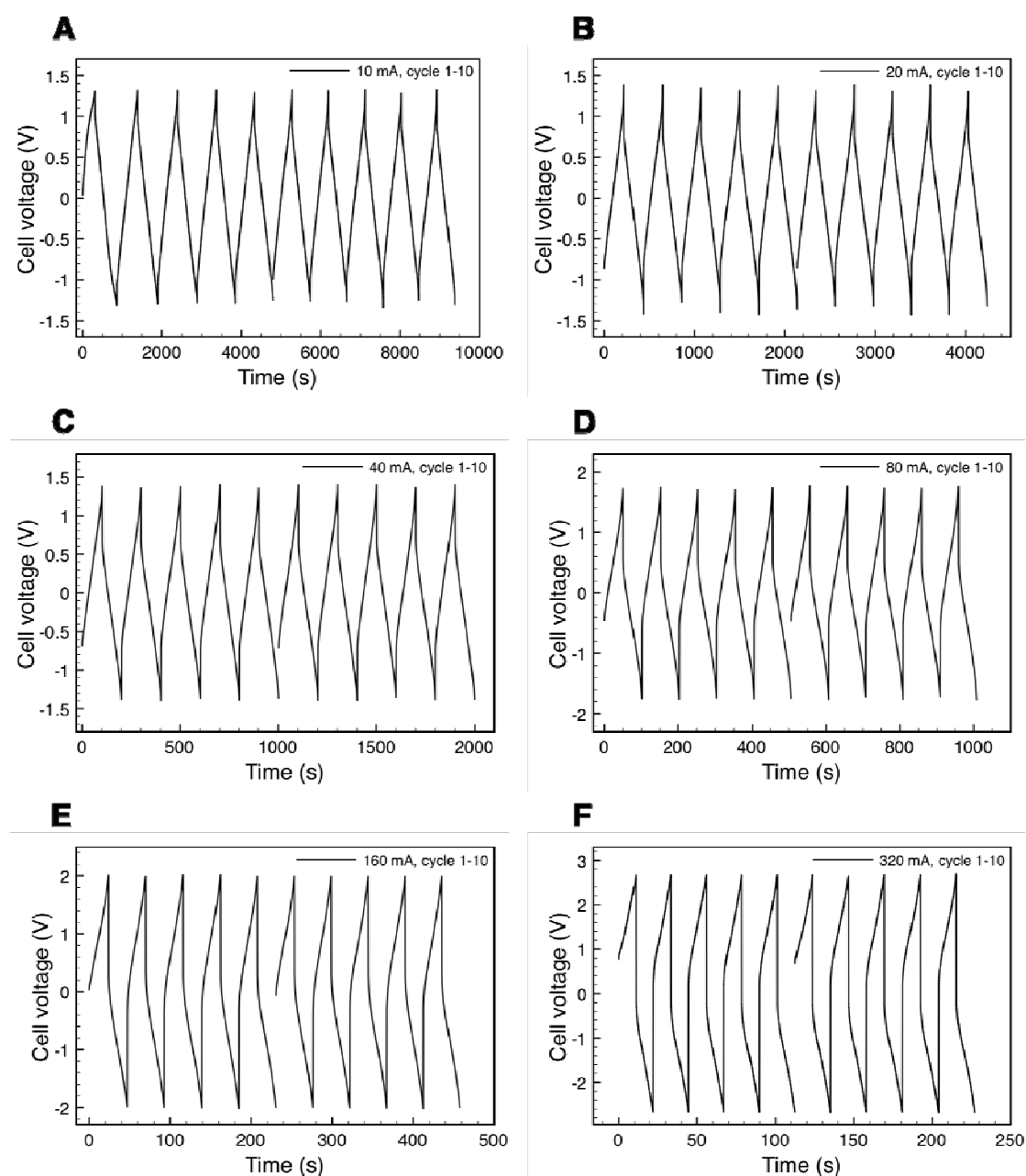
**Figure S2.** Schematic drawing of anion and electron transfer in PPy film during electrochemical red-ox switching.

**Figure S3** shows the cyclic voltammograms recorded at different scan rates for composite paper electrode under study in 2.0 M sodium chloride solution. The current in this graph was normalized with respect to the total mass of the conductive paper composite used as the sample. It is seen that the amount of charge passed during the red-ox process decreases as the magnitude of the scan rate is increased. Significant changes are observed in the cyclic voltammograms with respect to the positions of oxidation/reduction peaks, which is due to the larger  $iR$  drop at high scan rates.



**Figure S3.** Cyclic voltammograms of the composite conductive paper in 2.0 M sodium chloride solution from -0.9 V to +0.9 V for scan rates from 3  $\text{mV s}^{-1}$  to 20  $\text{mV s}^{-1}$ . Arrows indicate the direction of increased scan rate.

In **Figure S4** 10 consecutive charge-discharge curves of the battery cell at different charge currents are shown. The current was gradually increased from 10 mA up to 320 mA. Cycle number 7 at each current was used to evaluate the charge capacity for different current rates.



**Figure S4.** Charge and discharge cycles at different charge currents: 10 mA (A), 20 mA (B), 40 mA (C), 80 mA (D), 160 mA (E) and 320 mA (F). 10 cycles were performed for each current and the seventh of the cycles was used to evaluate the charge capacity in the report.

### Supporting References:

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