Manufacturing Poly(3,4-Ethylenedioxythiophene) Electro catalytic Sheets for Large-Scale H₂O₂ Production

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1. Introduction

Conducting polymers were discovered in the 70s by MacDiarmid, Heeger, and Shirakawa who were awarded the Nobel Prize in Chemistry in 2000.[1] They discovered that conjugated polymers, characterized with a chemical structure featured by an alternation between single and double bonds, are able to transport electrical charge carriers. This discovery is nowadays at the origin of new technologies and products on the market from antistatic coatings to transparent electrodes for solar cells and organic light emitting displays.[2,3]

The possibility to process conducting polymers from solution enables the use of printing technologies to create electronic and optoelectronic devices: known as printed electronics. Through chemical synthesis, it is possible to render a conducting polymer soluble in aqueous [4,5] or organic solution [6,7] by controlling the chemical nature of side chains of the main polymer chains. Another alternative is to complex a charged conducting polymer with a polyelectrolyte of opposite charge to create a stable suspension of nanoparticles.[8] This is the strategy used for the most used conducting polymer today: poly(3,4-ethylenedioxythiophene:poly(4-styrene sulfonate) (PEDOT:PSS).[9] Unlike films of small molecules or carbon nanostructures processed from solution, thin films of conducting polymers are often pinhole-free which is a prerequisite for solid state (opto)electronics to avoid electrical leakages. As mixed ionic and electronic conductors,[10] conducting polymers constitute the active material in thin-film based electrochemical devices, such as electrochromic displays,[11] electrochemical transistors and sensors,[12,13] and bioelectronic ion-pumps.[14] Today, technologies using conducting polymers are mostly based on thin films (<1 µm).

Conducting polymers offer various advantages as electrodes in electrochemical devices to replace rare and toxic metals, being composed of atomic elements of high abundancy.[15] Further, they are molecularly porous when swollen in an electrolyte and capable of transporting both ions and electrons, and possessing clean surfaces without insulating oxide layers, and still being corrosion-resistant in acids,[15] solution processability
enabling low-cost scalable manufacturing,[36] specific electrocatalytic activity.[37] Noteworthy promising applications, e.g., in fuel cells,[38] supercapacitors,[39] batteries,[40] and electrolyzers,[41] would rather require thick conducting polymer films (>10 µm).

However, the production of such thick electrode layers (10–100 µm) with good electronic (100 S cm⁻¹) and ionic (0.1 S cm⁻¹) conductivities is still a bottleneck to reach new electrochemical technologies. To fabricate thick layers of conducting polymers, i.e., paper-like sheets, for a roll-to-roll production is an important challenge. Chemical synthesis of a conducting polymer typically, produces a solution or a nanosuspension with solid content of the order of few % in weight. Removing ~90% of water and getting sheets of thickness between 10 and 100 µm is a major challenge. Note that high energy cost practically rules out large-scale evaporation. There exists a variety of filtration methods for various size of particles by applying a pressure on the feed liquid, such as microfiltration (particle size = 0.1–5 µm, P = 0.1–3 bar); ultrafiltration (particle size = 0.02–0.1 µm, P = 2–10 bar), nanofiltration (particle size = 0.001–0.02 µm, P = 5–30 bar). In general, the larger the particles the lower the pressure needed and the cheaper is the system and its operating cost. For mass manufacturing of conducting polymer electrodes for large volume supercapacitors or electrolyzers, utilization of paper machines with their wide wire mesh can be envisaged.

The purpose of this work is to design a process and to produce a thick PEDOT sheet for an electrochemical device with the help of large pore wire mesh starting from a diluted commercial aqueous solution of PEDOT:PSS. To this end, we destabilize the nanosuspension and induce its flocculation toward large microparticles. However, the soft microparticles formed lead to fouling of the wire mesh used in a sheet manufacturing. The introduction of carbon microfibers into the slurry enables the spontaneous formation of porous aggregates in the sheet that reduce the dewatering time by two orders of magnitude, down to seconds with a pore size typical of a paper machine. The PEDOT-carbon fiber aggregate obtained is rather inhomogeneous, however, as demonstrated by its test as electrode for the reduction of dioxygen to H₂O₂, this is not an obstacle for its function.

2. Results and Discussions

2.1. Formation of Conducting Polymer Microparticles

Our starting point is a previous observation that 1 M sulfuric acid solution is destabilizing a nanosuspension of PEDOT:PSS.[22] Moreover, treatment of PEDOT:PSS with sulfuric acid by dipping the film[23] or exposing it to vapor[24] as well as addition of sulfuric acid to PEDOT:PSS water suspension was observed to lead to an increased conductivity.[25] The mechanism proposed is the ion-exchange between the anions of the acids and the PSS that induced a phase separation of the excess insulating PSS chains and the establishment of a three-dimensional conducting network in the film.[26] Here, we investigated this phenomenon further.

We follow the evolution of PEDOT colloidal particles sizes when treated with H₂SO₄ by dynamic light scattering (DLS). The onset of the decay of DLS correlograms depends on the average particle size: it shifts to larger times with increasing particle size. Figure 1a shows the correlogram of the sample containing 1 mL of PEDOT:PSS (C = 2.7 g L⁻¹) and 2.64 mL of 1 M H₂SO₄ (C = 0.72 m). Within a few minutes, after H₂SO₄ is added to the PEDOT:PSS water suspension, an approximately two orders of magnitude shift toward longer correlation time is observed, indicating that PEDOT particles undergo a fast flocculation leading to an increase of particle size by about 100 times. The flocculation leads to particles of the order of 100 microns in size and some are still suspended in the solution after 18 h (green curve, Figure 1a); but most of them have grown so big that they precipitate (Figure 1c). The PEDOT:PSS particles in the water suspension consist of a core of positively charged PEDOT chains neutralized with PSS anions surrounded by a hydrophilic shell composed of negatively charged PSS chains (Figure 1b).[27] The negative charges of the sulfonic acid groups on the shell promote an electrostatic repulsion of the PEDOT-PSS and thus a stable suspension. The average particle size is typically in the submicron
2.2. Filtration Process of PEDOT Microparticles

We are now looking into the formation of a free-standing layer by vacuum filtration (VF) of the PEDOT microparticles formed after flocculation in sulfuric acid. We keep the duration of the acid treatment to 1 h, but the acid concentration is systematically varied (18, 10, 5, 0.5, and 0.1 M), as the flocculation kinetics depends on it. The flocculation leads to a precipitation of microparticles of PEDOT that looks like a slurry or a paste at the bottom of the vessel. We put the content of the vessel on a filtration unit equipped of plastic wire mesh of 60 µm pore size (Figure 2a). After pumping to help the dewatering, a free-standing layer of PEDOT is formed. The thickness of the layer made is typically in the range from 60 to 500 µm and depends on the amount of PEDOT microparticles used.

Upon filtration on the wire mesh, oversize particles in the feed cannot pass through the lattice structure of the wire mesh, while fluid and small particles pass through, becoming filtrate. The UV-vis-NIR spectra of the filtrate (Figure S3, Supporting Information) reveal two absorption features, one peak at 225 nm related to the optical transition in PSS[30] and one broad absorption in the near-infra red with a peak at 900 nm; which is attributed to Drude-like absorption of PEDOT.[15] Figure 2b summarizes the absorption intensities versus sulfuric acid concentration. For low concentration (<0.5 M), PEDOT:PSS particles are smaller than the pore size of the wire mesh and they pass through. For higher concentrations, the amount of PEDOT in the filtrate decreases and becomes almost negligible above 5 M as indicated by a decrease of both absorption contributions. Importantly, at high concentration (95%), no absorption of PEDOT is visible anymore in the filtrate, but a clear absorption feature of PSS remains. This later observation is an indication that the sulfate and hydrogen sulfate anions in fact have been exchanged with PSS in the PEDOT microparticles blocked by the wire mesh, and that the PSS has been dissolved in the solvent and detected in the filtrate. Those measurements support the proposed model in Figure 1b.

After the PEDOT soft sheets are further dried on a hot plate and easily delaminate from the wire mesh. The conductivity varies from 20 to 100 S cm\(^{-1}\) upon increasing the concentration of the acid treatment. We explain these trends by the removal of the insulating PSS from PEDOT:PSS that is enhanced by the anionic concentration in sulfate and hydrogen sulfate. Although thin films of PEDOT:PSS on a substrate can reach one order of magnitude higher conductivity,[31] the PEDOT sheets obtained here have comparable electrical conductivities compared to other methods forming free-standing PEDOT sheet by simple water evaporation.[10]

2.3. Improving the Dewatering Mechanism

We now turn to the issue of scalability and production rate of PEDOT sheets. While VF with a pressure of 10 mbar is quite efficient in a small set-up, it is not appropriate for large roll-to-roll manufacturing. Commercial machines for dewatering are either equipped with VF, such as a rotary vacuum filter drum[32] or use an applied pressure, such as belt filter[33] In...
both cases, the pressure difference is relatively little; hence we use as a simple set-up for the dewatering that is a sheet former (Figure S4, Supporting Information). The paste of PEDOT microparticles (1 m H₂SO₄) in water was used as the feed for the sheet former using a wire mesh of 60 µm pore size. Hence, gravity of water/slurry is the perpendicular force applied to the wire mesh in this batch filtration unit (sheet former). The PEDOT microparticles in the slurry are big, soft, and likely impermeable, such that they simply clog the wire mesh while very little PEDOT is found in the filtrate. Hence the first layer of the cake is quickly formed and water does not pass through anymore, a phenomenon known as dead-end filtration.

To avoid wire mesh fouling and accelerate dewatering, we explore the effect of adding different types of carbon fibers with the hope that interconnected voids/porosity in the cake would improve water permeability. Carbon fibers contain at least 92 wt% of carbon, while fibers containing at least 99 wt% are named graphite fibers.[34] They are well known for their excellent tensile properties, low densities, high thermal and chemical stabilities, electrical conductivities, and creep resistance. Carbon fibers used in this study are: (1) graphitized polyacrylonitrile fibers (G-CF) without and with epoxy resin sizing/coating treatment and (2) high Young modulus anisotropic/mesophase pitch (CF). These fibers have an average diameter of ~7 µm. Fibers are tested in the small-scale experiments (filtering area of diameter = 1.5 cm) with 5 mL of commercial PEDOT:PSS (Fibers/PEDOT = 270% and PEDOT weight = 18.5 mg) before proceeding to industrial scale. Figure 3a displays the measurement of reciprocal of rate at which water passes through the wet PEDOT-CF layers, called the cakes. The cake resistance (αₐ) is extracted from the slope of reciprocal of filtration rate (t/V) versus water volume using Darcy’s equation.[35,36] Table 1 compares the dewatering time and specific cake resistance (αₐ) calculated using constant pressure modeling of PEDOT₁M (PH1000 treated with 1 m H₂SO₄) films in steps: 0 mg CF, 11 mg CF, 20.5 mg CF, 50 mg CF, 50 mg pulp, 50 mg G-CF₁ (no sizing treatment), and 50 mg G-CF₂ (epoxy sizing treatment to improve wettability) using constant pressure modeling. Figure 3a clearly demonstrates that with the right amount of CF/G-CF₁, the overall filtration performance could be enhanced. Initially, the addition of 11 mg CF does not influence the filtration performance. However, with further addition of 20.5 mg CF, the rate of water removal increases; and with 50 mg CF, the cake resistance αₐ decreases by one order of magnitude. The comparison between the various fibers (50 mg of CF, G-CF₁, G-CF₂) reveals that not only the type but also the sizing treatment of the fibers effect dewatering process. With G-CF₂, the cake is completely blocking the liquid flow and the filtration becomes very slow. We suspect that the epoxy-coating on the CF[37] is partially dissolved in the acidic treatment and/or interacting with the PEDOT particles to form a very dense cake.

The visual observation of the layers reveals that the CF aggre- gate in domains that look like protrusions (Figure 4a). Because of that the layers do not look homogenous but the dewatering is efficient. X-ray microtomography analysis is used to study internal microstructure porosity and morphology changes on PEDOT₁M upon the introduction of the CF. Figure 4b represents the 3D image of free-standing PEDOT₁M layer (~0.5 mm thick) revealing a dense bulk material that causes low flux of
water. The introduction of 50 mg CF in the PEDOT layer creates porous channels (white fibers, in Figure 4c) inside the composite responsible for the dewatering.

We have made some attempts to increase the dispersion of the CF and improve the homogeneity of the layers. For that purpose, environmentally friendly and easily decomposable biopolymers such as cellulose acetate (CA) and gelatin are mixed in PEDOT1M + CF composites. CA and gelatin are well known to improve the dispersion of carbon nanotubes,[38,39] hence we expect that they will also provide good interaction with the large CF and help the homogenization of the layer. Figure 3b shows the variation of \( \alpha_m \) with composite materials containing no fibers, only CF, and fibers with above mentioned biopolymers. It is observed that even with high amount of CA addition of 0.36 g (CA/PEDOT = 363 wt%, CA/CF = 545 wt%), CFs are not efficiently distributed (Figure S6, Supporting Information), but an addition of 0.2 g gelatin (gelatin/PEDOT = 201 wt%, gelatin/CF = 303 wt%) causes uniform distribution of CF (Figure S6c, Supporting Information). However, solving the dispersion of CF leads to slow dewatering. Based on those results, it is safe to conclude that aggregation of CF in those composite layers, as illustrated in Figure 4b, promotes the dewatering process fast by providing opening channels. On the other hand, dispersion of individual CF surrounded by bulky PEDOT microparticles tends to hinder water flow.

Based on its fastest dewatering, the pitch-based anisotropic fibers are chosen for the rest of the study. Figure 3c shows the influence of CF on the average conductivity of PEDOT 1M composite films. The error bars are large because of the CF rich areas that look like protrusions. The conductivity is about 40 S cm\(^{-1}\) for the PEDOT1M layer (dry cake). The addition of 6.5 mg CF does not change its conductivity; and adding more CF (11 and 20.5 mg) only slightly decreases the conductivity. Figure S5 (Supporting Information) shows in detail the \( \sigma \) measured for each of the added CFs. The slight decrease in conductivity is likely due to the creation of more protrusions of CF domains but they do not ruin the conductivity, which means that those layers will be interesting porous electrodes for electrochemical applications.

### 2.4. H\(_2\)O\(_2\) Production

There is active development of metal free-catalysts for electrochemical oxygen reduction and production in particular.[40,41] Here, we explored electrochemical kinetics of H\(_2\)O\(_2\) electrochemical production from the oxygen reduction reaction on free-standing thick PEDOT-CF electrodes obtained in the previous section by the filtration technique. We introduce the PEDOT-CF electrodes in double compartment cell with salt bridge Figure 5a. We want first to comment on the ability of the carbon fibers and the PEDOT part in the composite to drive the oxygen reduction reaction and peroxide production. PEDOT film coated glassy carbon electrodes are known to be efficient heterogeneous catalysts for the direct reduction of oxygen into hydrogen peroxide following a two-electron mechanism.[42] The carbon electrodes are known to provide higher overpotential and lower current density for the oxygen reduction reaction compared to PEDOT.[43] Hence, the contribution from the carbon fibers in the production of H\(_2\)O\(_2\) is expected to be negligible.

Both PEDOT1M electrode layer and PEDOT-CF electrodes clearly showed an ability to drive electrosynthesis of hydrogen.

| Compositions | \( \alpha_m \) [m kg\(^{-1}\)] | Filtration performance |
|--------------|-------------------------------|-----------------------|
| 0 g CF       | \( 4.82 \times 10^9 \)       | Slow                  |
| 11 mg CF     | \( 3 \times 10^9 \)          | Slow                  |
| 20.5 mg CF   | \( 1.01 \times 10^9 \)       | Moderately fast       |
| 50 mg CF     | \( 6.94 \times 10^8 \)       | Moderately fast       |
| 50 mg G-CF1  | \( 2.7 \times 10^9 \)        | Slow                  |
| 50 mg G-CF2  | \( 3.3 \times 10^{10} \)     | Very slow             |

Figure 4. a) Images of a PEDOT cake including some CF and forming a large protrusion. b) X-ray microtomography 3D images with a field of view of 0.7 mm of b) PEDOT1M layer; c) PEDOT1M layer including 50 mg fibers.
peroxide. Those macroscopic electrodes lead to a steady-state production efficiency of more than 40% (Figure 5c) after 40 min from the electrolysis start. This suggests a complex dynamic process on the freestanding electrodes. The H$_2$O$_2$ product concentration showed a linear growth with time reaching $0.2 \times 10^{-3}$ m after an hour of electrolysis (Figure 5b). The addition of CF did not have a significant effect on the production rate of H$_2$O$_2$. Hence, the presence of big aggregates seen as protrusions did not deteriorate the electrochemical activity of the electrodes, while the formation of CF aggregates with their channels in the dispersion significantly improved the dewatering process and thus the manufacturing time for those electrodes.

3. Conclusions

Given proven high promise of conducting polymers as electrode materials in electrochemistry, in this work, we tackled the task of producing a thick PEDOT-containing sheet starting from a stable aqueous nanosuspension of PEDOT:PSS. In the first step, the nanosuspension was flocculated with sulfuric acid to produce a slurry of conducting polymer micro-particles. However, filtering the latter out from the supernatant proved to be time and energy consuming because of the clogging of its soft micro-particles on the wire mesh. Taking into account that a prospective electrode material needs to be electrically conducting and that filter fouling needed to be avoided; we considered the addition of carbon fibers to introduce porosity to accelerate dewatering, while retaining electrical conductivity in the composite. Indeed, the permeability of water through the interconnected voids/porosity of this composite cake made possible its dewatering within seconds at a wire mesh with a pore size typical of a paper-machine with low differential pressure applied. The formation of carbon fiber aggregates leads to protrusion in the layer that did not affect much its electrical conductivity ($40$–$20$ S cm$^{-1}$), neither its electrochemical activity. Indeed, the 0.5 mm thick PEDOT/carbon fiber composite electrode was tested in an electrolyzer for producing hydrogen peroxide by oxygen reduction. Apparent nonuniformity of the conducting polymer distribution throughout the composite electrode was not an obstacle to obtain the performance of the same amount of pure PEDOT, thus suggesting that electrical contact is well assured by the carbon fiber network. Hence, we succeed to make a manufacturing process significantly decreasing the dewatering time, which is essential in mass production of electrodes and industrialization of large electrolyzers for H$_2$O$_2$ production. H$_2$O$_2$ is seen as a promising fuel and green chemical very popular in the trend of sustainable industrial processes.

4. Experimental Section

Materials: Poly(3,4-ethylenedioxythophene):poly(styrenesulfonate) (PEDOT:PSS), Clevios PH 1000, was purchased from Heraeus. Sulfuric acid (H$_2$SO$_4$) with nominally 95–98%, CA, and gelatin were purchased from Sigma Aldrich. Table 2 shows the fibers used in this research work.

Cake Formation Process and Filtration Modeling: VF method, using single unit membrane pump, was employed to form free-standing thick films (~0.5 mm) from microparticles slurry using filter paper pore sizes ranging from 30 to 330 µm. Integrated constant pressure model (integration of pressure drop across cake with the boundary conditions $t = 0, \nu = 0$, and $t = t, \nu = t$) was employed to study the specific resistance of those filtered cakes to the flow of filtrate using Equation (1), where $\alpha_m$ is the normalized specific cake resistance, $\nu$ is the filtrate volume and $t$ is the filtrate time, $b$ is the slope of filtration rate ($t/\nu$) versus volume.

![Figure 5](image-url)
change plot, \( A \) is the area of the filter, \( c \) is the mass of solids per unit volume filtrate pressure, and \( \mu \) is the dynamic viscosity

\[
\alpha_m = \frac{2bA}{Pc\mu}
\]

(1)

\( \alpha_m \) is lower for fast filtration systems. Note that generally, this model involves continuous growth of material cake on top of a filter to evaluate specific cake and filter medium resistances. However in this case, since the cakes from PEDOT microparticles slurry were present from the initial stage and not continuously growing therefore only specific cake resistances were taken into consideration. The experimental set-up consisted of a VF assembly with a funnel capacity of 15 mL. Deionized water was slowly poured in a controlled manner on top of those cakes. Filtrate time and volume were recorded using timer and weighing scale, respectively, as the clean water passed through the filter medium.

**Measurements:** Film resistances were measured using a Keithley 2400 source meter in four-wire sense mode. Strips of the samples of known width (2 mm) were pressed on four gold electrodes to ensure stable electrical contact. Thickness of the samples was measured using a micrometer screw gauge. The conductivity of the samples was calculated using Equation (2), where \( R \) is the resistance, \( t \) is the thickness, \( \omega \) is the width, and \( L \) is the length of the samples.

\[
\sigma = \frac{L}{R\omega t}
\]

(2)

**DLS Measurements:** DLS measurements were performed using an ALV-CGS-5022F goniometer system (ALV GmbH, Langen) with a 22 mW 633 nm HeNe laser. Sample solutions were prepared by mixing 1 mL of PEDOT:PSS water dispersion (1.3 wt%) and 2.64 mL of 1, 0.1, and 0.01 m of diluted H\(_2\)SO\(_4\). A total of 10 mm diameter cylindrical glass cuvettes containing the samples were immersed in a refractive index-matching toluene bath. The toluene was temperature-controlled to 22 \(^\circ\)C. The DLS system operates in pseudo-cross-correlation mode, with scattered light collected into a near single-mode optical fiber, subsequently split to two avalanche photodiodes (Perkin-Elmer). The time correlation function of the scattered intensity was obtained from a dual multiple-tau correlator with 328 channels (ALV-6010-160).

**Electrocatalytic Generation of Hydrogen Peroxide by PEDOT Foils:** The cell of two compartments connected via salt bridge was used for the production of hydrogen peroxide.\(^{[40]}\) The free-standing PEDOT:PSS-based films (exposed geometrical area of 1 cm\(^2\)) and platinum wire were used as working and short-circuited counter-reference electrodes, respectively, in oxygen-saturated sulfuric acid as a background electrolyte (pH 2) with a constant current density of \(-0.25\) mA cm\(^{-2}\) controlled by a potentiostat Gamry Interface 1010B.

UV-vis assay was used for the quantification of hydrogen peroxide. Every 20 min 10 \( \mu \)L of electrolyte from cathode compartment was collected and added to 290 \( \mu \)L of freshly prepared horseradish peroxidase (HRP) and 3,3,5,5-tetramethylbenzidine (TMB) in phosphate-citrate buffer solution. Then the mixed sample was measured at a wavelength of 653 nm using a BioTek Synergy H1 Hybrid Multi-Mode Reader. Finally, the concentration of hydrogen peroxide was determined from the calibration line with known concentration (0, 10, 20, 30, and \( 40 \times 10^{-6} \) m) of hydrogen peroxide. The faradaic efficiency (FE) over time was calculated as:

\[
FE = \frac{2FCV}{It} \times 100\%
\]

(3)

where \( F \) is Faraday constant (96 485.3 A mol s\(^{-1}\)), \( C \) is the concentration of hydrogen peroxide (mol L\(^{-1}\)), \( V \) is the volume of the cathode compartment (L), \( i \) is the current (A), and \( t \) is the time duration (s).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that supports the findings of this study are available in the supplementary material of this article.

**Keywords**

conducting polymers, thick films, H\(_2\)O\(_2\) production, large-scale, fast dewatering, low-cost

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