Electrochemically Active Polymeric Hollow Fibers
based on Poly(ether-*b*-amide)/Carbon Nanotubes

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Electrochemically Active Polymeric
Hollow Fibers based on Poly(ether-*b*-amide)/Carbon Nanotubes

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Abstract

A simple and effective method to incorporate catalytic activity to a hollow fiber membrane is reported. Polyetherimide hollow fiber membranes were coated with a solution containing carboxyl-functionalized multi-walled carbon nanotubes and poly(ether-*b*-amide). Electron microscopy images confirmed the presence of a layer of percolating carbon nanotubes on the surface of the membranes. Cyclic voltammetry and linear swept voltammetry experiments showed that these membranes are able to drive the reactions of hydrogen evolution, and oxygen reduction, making them a cheaper, and greener substitute for platinum based cathodes in microbial bioelectrochemical systems. Water flux and molecular weight cut off experiments indicated that the electrochemically active coating layer does not affect the ultrafiltration performance of the membrane.

Keywords: hollow fibers, carbon nanotubes, electrochemical membrane reactors, poly(ether-*b*-amide)

1. Introduction

After a vast exploitation of nonrenewable resources like oil, natural gas, and coal, to meet the world's energy requirements one of its biggest challenges is finding a source and a process of energy conversion, which would not negatively affect the environment in the way current technologies do. The other primordial challenge is to supply clean water without depleting precious resources at the high rate currently being done.

Bioelectrochemical systems, microbial electrochemical technologies [1], emerge as green technologies, which simultaneously approach clean water and energy conversion [2-4]. They are constituted by electrochemical cells, which use exoelectrogenic [5] bacteria at the anode to catalyze an oxidation reaction. The electrons produced at the anode travel through an external circuit to the cathode, where a reduction reaction takes place. From this process, energy can be harvested as electricity, in a microbial fuel cell (MFC), or stored in renewable chemical fuels, in microbial electrolysis cells (MEC) [6, 7] (Figure 1). For the purpose of wastewaters treatment, the substrate to be oxidized can be the organic materials dissolved in them [3, 8], thus decreasing the chemical oxygen demand (COD) of the effluents.

Figure 1. Bioelectrochemical systems: organic waste is oxidized at the anode by the electrochemically active microorganisms, and electrons travel through an external circuit to the cathode. Electricity is in this way produced in a microbial fuel cell (MFC). If power is consumed to harvest chemicals, the device works as a microbial electrolysis cell (MEC) [8].

So far, bioelectrochemical devices have been successfully tested at laboratory scale, but there are only a few studies regarding their implementation at a bigger scale [9]. One of the bottlenecks in the scaling up of these systems is the cathode. The materials involved in its production, specially noble metals, are very expensive and not environmental friendly [10]. Between the materials considered more promising for these applications, and less harmful for the environment, are nickel and stainless-steel alloys [11]. Carbon based materials (e. g. carbon nanotubes, graphene, graphene oxide, carbon nanofibers among others), [12-14], are gaining attention, because of their surface area, electronic properties, easy availability, and low cost. These materials, pristine or modified, have been tested for ORR [15-19] and HER [20-23] with satisfactory results. Carbon materials along with different polymers have been combined in different ways in order to get electrochemical conductive membranes [24-31]. Carbon nanotubes have been also used as additive for conductive polymeric membranes for fouling prevention [32] or electrochemical removal of chromium from water [33]. Malaeb et al. [34] used a flat sheet polymer membrane mainly constituted by carbon nanotubes, which acted as cathode and ultrafiltration membrane in a microbial fuel cell, obtaining good results in terms of the quality of the effluent, compared to systems without an integrated filtration process. This membrane was able to drive the oxygen reduction reaction.

The integration of an ultrafiltration process can make bioelectrochemical systems more efficient. To improve scalability even more, changing the membranes geometry from flat-sheet to hollow fibers could be an excellent option, because of their higher productivity per unit volume, feature derived from high packing density and large surface area [35].

Recently Katuri et al. [1, 13] used fully metallic (nickel based) hollow fiber membranes in a device analogous to that described in Figure 2, which is referred as anaerobic electrochemical membrane bioreactor (AnEMBR). The AnEMBR was used to treat low organic strength solutions and produce biogas. The reactor could be operated during 70 days without changing or cleaning the membrane.

Figure 2. Schematic diagram of an AnEMBR with electron conductive hollow fibers as cathode. (1) hollow fibers bundle, (2) anode, (3) energy supply, (4) external resistor, (5) gas bag, (6) pressure sensor, and (7) pump. Adapted from [13].

While the AnEMBR proof of concept was demonstrated, when aiming application in large scale, more feasible and cost-efficient solutions are needed. Hollow fibers are the most attractive configuration, however polymers are much more convenient materials for their manufacture. The polymer processability is easier, pore control is more versatile and cost is lower than that of metallic analogs. Polymeric (e. g. polysulfone based) hollow

fibers have been used for decades in large scale for hemodialysis. In order to be used in bioelectrochemical devices, however, most organic polymers lack in electron conductivity and catalytic activity. We recently reported the manufacture of fluorinated polyoxadiazole hollow fibers coated with platinum (Pt) by atomic layer deposition and their application as cathode/membrane in an electrochemical membrane reactor [36]. The high thermal stability of polyoxadiazole was an advantage during the process of Pt deposition. The Pt coated polymeric hollow fibers are an effective alternative to fully metallic hollow fibers. The Pt thin layer provides the needed conductivity and high catalytic cathode activity. But even cheaper approaches are needed for the technological implementation of electrochemical membrane reactors in large scale. This was the motivation of this work. Here we chose polyetherimide to manufacture hollow fiber membranes with outer surface pore size in the ultrafiltration range. Polyetherimide hollow fibers can be easily manufactured in machines in several meters scale [37-39]. To provide the needed conductivity and electrochemical activity in this work a hybrid coating with poly (ether-*b*-amide) and multi-wall carbon nanotubes was applied. The system was evaluated by cyclic voltammetry.

2. Experimental

2.1. Materials

Polyetherimide (PEI, Ultem®) was provided by SABIC (Saudi Arabia). Carboxylated multiwalled carbon nanotubes (CNT) were purchased from Nanocyl (average diameter 9.5 nm, average length < 1 micron, and % -COOH functionalization < 4). Poly (ether-*b*-

amide), Pebax® MH 1657, was obtained from Arkema. Potassium phosphate monobasic (KH_2PO_4) and potassium phosphate dibasic (K_2HPO_4) used in the preparation of the buffer solution for electrochemical experiments were bought from Fisher Scientific. Potassium ferricyanide, sodium dodecyl sulfate (SDS), diethylene glycol (DEG) and N-methyl-2-pyrrolidone (NMP) and ethanol were purchased from Sigma Aldrich. MiliQ water was used for the preparation of all aqueous solutions.

2.2. Hollow fiber preparation

PEI hollow fibers were prepared by phase inversion in a spinning machine. The dope solution consisted of 17 wt% PEI dope solutions in 18 wt % DEG and 65 wt% NMP. The bore fluid had 90 % water and 10 % NMP. The coagulant bath was water. The fibers were cast with 6 cm air gap, using 1.5 bar pressure, dope flow rate 9 m/min and bore fluid flow rate 3 m/min.

2.3. Coating of membranes

A mixture of 70:30 ethanol:water was used as solvent for poly (ether-*b*-amide). A 3% copolymer solution was prepared by heating the mixture to 60 °C under reflux and stirring during 3 hours. Solutions containing 4%, 8%, 10%, 12%, and 14% CNT, based on poly (ether-*b*-amide) weight, were prepared, by dispersing first CNT in the solvent mixture, containing SDS. The homogeneous dispersion was mixed with the 3 % copolymer solution, leading to final 0.15 and 0.2 % copolymer concentrations. For an effective dispersion the CNT was ultrasonicated in different steps, by using a Q500 sonicator (Qsonica) at 50 % amplitude, with on-off pulses of 2-2 seconds (total energy of

around 87000 joules). CNT/copolymer dispersions were stirred at 300 rpm for at least 24 hours before using.

PEI hollow fibers with the lower tip sealed were immersed in the CNT/copolymer dispersion three times, during 10 s each, and left to dry after each coating during at least 20 min. They were kept dry.

2.4. Morphological characterization

The membrane morphology and the distribution of carbon nanotubes in the coating layers were investigated by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM).

The membranes were imaged with a Quanta 200 microscope using a voltage of 5 kV. The uncoated membranes were sputter coated with iridium. For membranes with CNT coating, there was no need for sputtering. For the cross section the fibers were fractured in liquid nitrogen.

For TEM, the membranes were cut with diamond knife in a LEICA EM UC6 ultramicrotome after being embedded in a low viscosity resin and imaged in a Titan FEI transmission electron microscope operating at 300 kV.

2.5. Electrochemical characterization

Cyclic voltammetry was carried out in a single chamber electrochemical cell to evaluate if the modified material is electrically conductive. 50 mM of potassium ferricyanide

$\text{K}_3\text{Fe}(\text{CN})_6$ was used as electrolyte in a phosphate buffer solution (100 mM; pH 7). In addition, cyclic voltammetry and linear swept voltammetry were carried out in a single chamber electrochemical cell in order to evaluate the performance of the developed cathode for ORR and HER. Phosphate buffer solution (100 mM; pH 7) was used as the electrolyte, with Ag/AgCl and graphite rod as reference counter electrode, respectively. Electrochemical measurements were carried out using a VMP3 potentiostat (Biologic). . To normalize the measured current, the values were divided by the effective surface area of the cathode.

2.6. Evaluation of the coating stability in water

The coated membranes were immersed in miliQ water during periods of 18 hours. After each immersion they were dried in the oven at 60 °C during 2 hours, then the weigh was measured to count the potential loss weight each time. The total time of immersion in water was 150 hours.

2.7. Water flux and molecular weight cut off (MWCO)

The water permeation was measured by promoting the water flow from outside to the lumen of the fibers. Experiments were carried out at different pressures, provided by nitrogen cylinders.

Seven solutions were prepared using poly(ethylene glycol) of different molecular weights: 0.3, 1.5, 6, 10, 35, 100 and 600 kg/mol. The set up for this test was the same used for water permeation. The MWCO is the minimum molecular weight, which is 90 % rejected.

3. Results and discussion

PEI hollow fibers were manufactured with pore size in the range of ultrafiltration, as characterized by FESEM and shown in Figure 3a. The fiber cross section is imaged in Figure 3b, indicating an outer diameter of 753 μm . The water flux of the uncoated PEI hollow fibers as a function of pressure is shown in Figure 4. The average water permeance was $113.0 \text{ Lm}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, measured at 2 bar. The MWCO measured with poly (ethylene glycol) was around 70 kg/mol, as seen in Figure 5. For coating the solvent used was a mixture of 70:30 ethanol:water, which could be considered a green system. The coating had the objective of adding electrochemical activity to the membranes, keeping high flux and ultrafiltration properties. Therefore coating was promoted with diluted poly (ether-*b*-amide) solutions (0.15-0.20 wt %), which should be diluted enough to avoid pore blocking. CNT was added in different amounts up to 14 wt % in relation to the polymer weight. Due to the carboxylic functionalization the CNT could be effectively dispersed in the poly (ether-*b*-amide) /water/ethanol solution. Addition of sodium dodecyl sulfate (SDS) [40] improved even more the dispersion. Figure 3c confirms that pores are still open after coating. The dispersed carbon nanotubes are clearly imaged in the same micrograph. The thin layer of carbon nanotube coating onto the PEI hollow fiber is imaged by TEM in Figure 3d. The width of the coating layer is approximately 60-70 nm. Figure 4 shows that only slight change of flux is observed after coating. The values of MWCO are kept after coating in the range of ultrafiltration, between 70 and 80 kg/mol (Figure 5).

The evaluation of the stability of the coating layer was then evaluated. The weight of coated membranes was measured before and after 150 hours in water was constant. The membrane is stable in water.

Figure 3. Morphology characterization. FESEM of (a) uncoated PEI fiber surface; (b) cross section of PEI hollow fiber; (c) coated membrane surface and TEM of (d) coated membrane surface.

(a)

(b)

Figure 4. Water flux as a function of pressure for a PEI hollow fiber before and after coating with a 0.15% poly (ether-*b*-amide) solution containing 0.012 % CNT (8% CNT to 92 % copolymer).

Figure 5. Rejection of poly(ethylene glycol) of different molecular weights tested for hollow fibers before coating (U) and after coating with poly (ether-*b*-amide) solutions containing different ratios (4 to 14 wt %) of CNT relative to the copolymer.

From the results above it was confirmed that the hollow fibers have suitable characteristics for ultrafiltration also after coating with CNT/poly (ether-*b*-amide). Therefore it could be used in classical membrane bioreactors for water treatment. The main objective of this work is however to propose simple cost-effective membranes for electrochemical bioreactors. The electrochemical activity of coated membranes (8 to 14 wt % CNT relative poly (ether-*b*-amide)) was then evaluated by cyclic voltammetry (CV) and linear-sweep voltammetry (LSV) measurements.

Electrochemical characterization

Figure 6. Cyclic voltammetry with typical response for a hollow fiber coated with poly (ether-*b*-amide) and 8 % CNT.

Figure 7. (a) LSV (ORR evaluation) for a membrane coated with poly (ether-*b*-amide) and 10-12 % CNT (relative to copolymer), and (b) LSV (HER evaluation) for coated fibers with 4-14 % CNT. All electrochemical experiments were carried out in a hot (30°C) under no light exposure.

The results of electrochemical activity evaluation are shown in Figure 6 and 7. The CV results demonstrate that the coated fibers with at least 8 % CNT are electron conductive, indicating that CNT percolate with adequate distribution. Furthermore electrochemical characterization was performed to evaluate the ability of driving oxygen reduction reaction (ORR) of membranes. After converting the potential to RHE, the reduction peak in figure 7a can be ascribed to the reduction of oxygen to hydroxide [41]. Results are illustrated for 10 and 12 % CNT (Figure 7a). At more negatives values of potential (Figure 7b), the response of linear swept voltammetry shows an onset potential close to

the thermodynamic potential of the HER, indicating that these CNT-COOH coated membranes are able to drive the reaction, as it has been already reported for cathodes modified with different functionalized CNTs [42,43]. Results are presented for different CNT ratios indicating that at more CNT load, the kinetics of the reaction is improved.

4. Conclusions

Electrochemical activity was added to the PEI hollow fiber membranes by incorporating a thin coating layer in the outer surface, based on poly (ether-*b*-amide) and CNT. We confirmed that the electrochemical active fibers prepared by the proposed method could drive reactions on hydrogen evolution and oxygen reduction. The hollow fibers have high porosity, which is maintained after coating to allow efficient performance in ultrafiltration. The water flux is around $113 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with molecular weight cut-off around 70-80 kg/mol. The coating stability in aqueous medium was confirmed. With the combination of ultrafiltration performance and electrochemical activity we believe that this system could have application in bioelectrochemical membrane reactors at a relatively low cost. Additional catalytic activity could be incorporated for instance by using metallic salt dispersed in the coating solution, followed by reduction and generation of catalytic nanoparticles. The scaling up could be easily done requiring regular machines used for commercial membrane manufacture.

5. Acknowledgement

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Graphical Abstract

Highlights

Electrochemically Active Polymeric Hollow Fibers as
Cathode for Bioelectrochemical Systems

Carolina Cuevas, Dooli Kim, Krishna P. Katuri, Pascal Saikaly and Suzana P. Nunes★

- Electroconductive polymeric hollow fibers
- Membrane-based bioelectrochemical system demonstrated
- Poly(ether-b-amide)/carbon nanotubes coated hollow fibers