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Electrochemically active polymeric hollow fibers based on poly(ether-*b*-amide)/carbon nanotubes

Carolina Cuevas[a], Dooli Kim[a], Krishna P. Katuri[b], Pascal Saikaly[b], Suzana P. Nunes[a,*]

[a] King Abdullah University of Science and Technology, Biological and Environmental Science and Engineering Division, 23955-6900 Thuwal, Saudi Arabia
[b] King Abdullah University of Science and Technology, Biological and Environmental Science and Engineering, Water Desalination and Reuse Center, 23955-6900 Thuwal, Saudi Arabia

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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.

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] (Fig. 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.

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

* Corresponding author.
E-mail address: suzana.nunes@kaust.edu.sa (S.P. Nunes).

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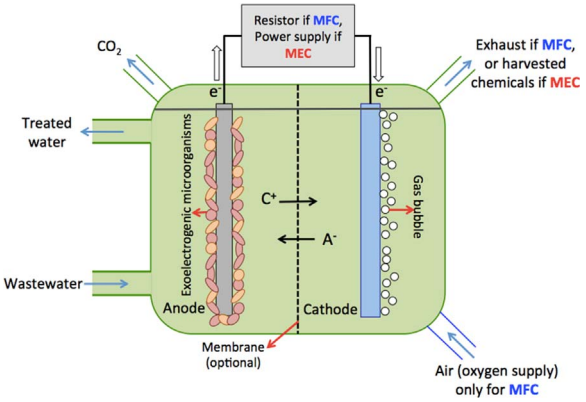

Fig. 1. Biolectrochemical systems:organic waste is oxidized at the anode by the electrochemically active microorganisms, and electrons travel trough an external circuit to the cathode. Electricity is in this way produced in a microbial fuel cell (MFC). If power is consumed to harvest chemicals, the device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

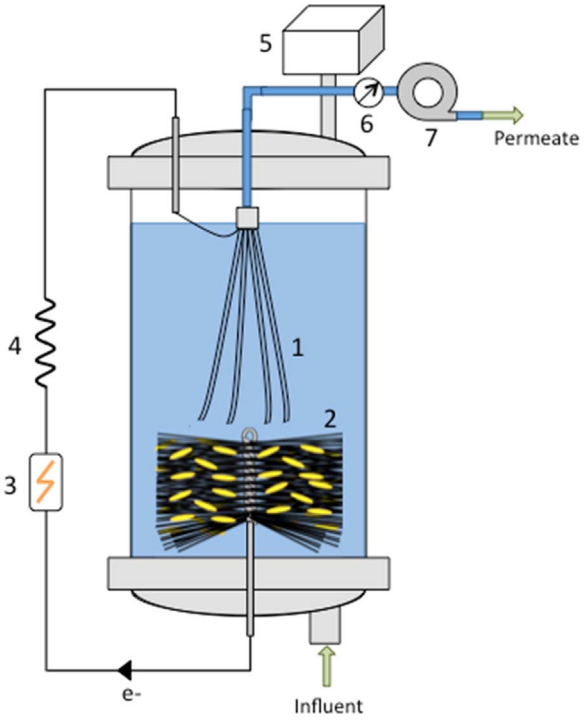

Fig. 2. Schematic diagram of an AnEMBR with electron conductive hollow fibers as cathode. (1) hollow fibers bundle, (2) anode, (3) energy supply, (4) external resistor, (5) gas bag, (6) pressure sensor, and (7) pump. Adapted from [13].

based) hollow fiber membranes in a device analogous to that described in Fig. 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.

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 biolectrochemical 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 lenght < 1 μm, 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 h. 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 s (total energy of around 87,000 J). CNT/copolymer dispersions were stirred at 300 rpm for at least 24 h 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).