

Short communication

# Layer-by-layer films of chitosan, poly(vinyl sulfonic acid), and platinum for methanol electrooxidation and oxygen electroreduction

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## Abstract

We describe an approach for manipulation of biodegradable chitosan and poly(vinyl sulfonic acid) (PVS) in layer-by-layer (LBL) film adsorbed onto gold via ionic attraction.  $\text{H}_2\text{PtCl}_6$  was deposited onto the LBL film, with chitosan/PVS layers serving as templates to yield metallic platinum. In electrochemical experiments this LBL film exhibited electrochemical stability, low permeability to methanol and conduction/diffusion of proton to maintain the electrolytic connection. The Pt/chitosan/PVS electrode also displayed electroreduction of molecular oxygen. With these features, this Pt/chitosan/PVS film may be used between the catalyst layer and the proton exchange membrane (PEM) in direct methanol fuel cells (DMFC) and biofuel cells.

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## 1. Introduction

Direct methanol fuel cells (DMFC) are expected to become important power sources for transport and portable applications due to their high energy density and simplified design [1–4]. The commercialization of DMFC and micro DMFC is hampered, though, by the high cost of the platinum catalyst, and this has motivated investigation into the electrocatalysis of novel materials for oxygen reduction reaction (ORR) [5–7]. A conclusion from such studies is that the use of platinum may be mandatory, and therefore much effort has been dedicated to obtain a material configuration of minimum Pt loading which maintains high electrocatalytic efficiency. Another drawback of DMFC is methanol oxidation at the platinum cathode due to the methanol crossover through the Nafion membrane, which is normally employed in these power sources. This promotes depolarization of the cell [8]. Therefore, it would also be

interesting if cathode materials were found to prevent such effects.

Membrane-electrode assemblies for proton exchange fuel cells (PEMFC) are produced with several methods [9–12]. Impregnating electrodes with solubilized perfluorosulfonic ionomer and Nafion® allows the fabrication of electrodes for phosphoric acid fuel cells with a 10-fold decrease in the catalysis loading while maintaining a good performance [13]. A catalyst layer was also prepared by mixing the solubilized ionomer with carbon supported platinum [14]. Another possibility to reduce the amount of Pt is to employ the layer-by-layer (LBL) technique [15,16], based on physical adsorption of oppositely charged layers, through films with metallic particles can be produced.

In this work we investigate the electrochemical properties of a novel electrode formed with the LBL method, with the architecture of Pt/chitosan/poly(vinyl sulfonic acid) (PVS). The aim is to exploit the control of LBL architectures to enhance the catalytic efficiency of Pt for the oxygen reduction reaction (ORR) and to avoid electrooxidation of methanol. Such material can in principle be used in a membrane-electrode assembly for a micro DMFC. Chitosan was chosen as a catalyst support, with added

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advantages for a micro DMFC: it shows low permeability to methanol, it does not expel pollutants as overheated up to 200 °C and does not pollute when discarded [17,18]. Furthermore, it can be incorporated in humans and plants into biofuel cells. Moreover, PVS was used in LBL with chitosan for obtaining a small hydrophobic/hydrophilic separation between polymeric N-bases and polymeric sulphonic acids. Thus, less connected hydrophilic channels can be obtained to reduce the methanol permeation while maintaining high proton conductivity [19–21].

## 2. Experimental

Layer-by-layer films were assembled onto gold-coated glass substrates. The LBL films were obtained via ionic attraction of oppositely charged materials, by the alternated immersion for 1 min of the substrate into the chitosan and poly(vinyl sulfonic acid) dispersions. Chitosan and PVS were purchased from Galena Química e Farmacêutica Ltda (Brazil). The concentration of these dispersions was 1.6 g L<sup>-1</sup>. After deposition of each layer, the substrates were rinsed for 30 s in HCl solution (pH 2) and dried under a nitrogen flow. A 10-bilayer LBL film of chitosan/PVS was placed in a 0.1 mol L<sup>-1</sup> H<sub>2</sub>PtCl<sub>6</sub> (Aldrich) solution during 1 min. After deposition of H<sub>2</sub>PtCl<sub>6</sub>, the substrates were rinsed for 2 s in HCl solution (pH 2) and dried as cited above. The H<sub>2</sub>PtCl<sub>6</sub>/chitosan/PVS electrode was placed in an electrochemical cell and polarized at 0.05 V for 1 min. The electrolytic solution was an aqueous solution of HClO<sub>4</sub> (pH 2.0). This procedure yields metallic platinum inside the chitosan/PVS matrix. In other words, the chitosan/PVS layers serve as biodegradable reactor for the fabrication of platinum. In the electrochemical experiments carried out with an Autolab PGSTAT30 potentiostat/galvanostat, the counter electrode was a platinum sheet with an area of 2 cm<sup>2</sup> and the reference electrode was the reversible hydrogen electrode (RHE).

## 3. Results and discussion

Fig. 1 shows the 2nd, 20th and 500th voltammetric cycles for the Pt/chitosan/PVS electrode at 10 mV s<sup>-1</sup>, after the H<sub>2</sub>PtCl<sub>6</sub>/chitosan/PVS electrode was dipped into the electrolytic solution at 0.05 V for 1 min. The electroreduction from PtCl<sub>6</sub><sup>2-</sup> to Pt is confirmed by the typical hydrogen adsorption/desorption profile, in the potential range below 0.3 V, of platinum electrodes [22,23]. The formation of the platinum on the substrate demonstrates that the chitosan/PVS LBL film acts as a biodegradable catalyst support. The Pt/chitosan/PVS electrode displays stable potentiodynamic responses under the conditions employed, as demonstrated by the small difference between the 2nd and the 500th voltammograms. The complexation between chitosan and the metallic particles maintains them fixed in the host matrix, which is essential for an electrocatalyst in a DMFC. Nevertheless, this complexation probably blocks some platinum sites for hydrogen adsorption/desorption, which is the reason for the less defined redox pair at 0.15 V.

Fig. 2 shows the linear scanning of the potential for the Pt/chitosan/PVS electrodes (dotted line) in perchloric acid solution (pH 2) with methanol (0.1 mol L<sup>-1</sup>) at 10 mV s<sup>-1</sup>. The onset

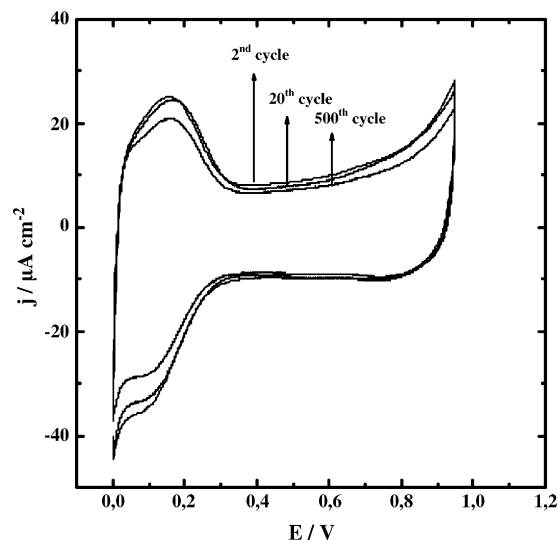


Fig. 1. Second, 20th and 500th cyclic voltammograms for the LBL films of Pt/chitosan/PVS in an aqueous solution of HClO<sub>4</sub> (pH 2.0);  $v = 10 \text{ mV s}^{-1}$ .

of methanol oxidation is at ca. 0.45 V, which can be inferred by comparing the voltammograms in the presence and absence of methanol. Fig. 2 also shows the linear scanning of the potential for another 10-bilayer LBL film of chitosan/PVS adsorbed on the Pt/chitosan/PVS electrode (full line). The onset of methanol oxidation is shifted to ca. 0.54 V, i.e. there is a 90 mV shift for more positive potentials, which is probably due to the low permeability to methanol in the chitosan/PVS layers. The LBL films of chitosan/PVS appear to cause a decrease in the methanol diffusion from the anode to the cathode through the PEM, which depolarizes the DMFC.

Fig. 3 shows the plots for the linear scanning of the potential for a Pt plate (dotted line) and the LBL chitosan–Pt electrode (full line) in the same electrolytic solution as in Fig. 1, and under a flux of oxygen. The sweep rate was kept at 10 mV s<sup>-1</sup>

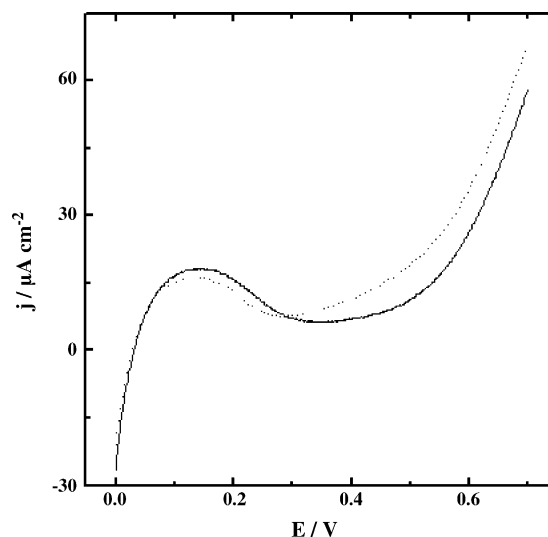


Fig. 2. Potential linear scanning for the LBL film of Pt/chitosan/PVS (---) and the 10-bilayer LBL film of chitosan/PVS adsorbed on the Pt/chitosan/PVS electrode (—) in an aqueous solution of HClO<sub>4</sub> (pH 2.0) with methanol (0.1 mol L<sup>-1</sup>);  $v = 10 \text{ mV s}^{-1}$ .

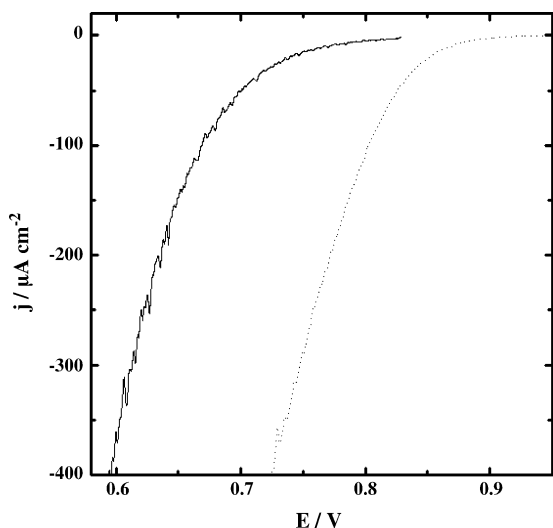


Fig. 3. Potential linear scanning for a Pt plate (---) and the LBL Pt/chitosan/PVS electrode (—) in an aqueous solution of  $\text{HClO}_4$  (pH 2.0) under  $\text{O}_2$  flux;  $v = 10 \text{ mV s}^{-1}$ .

to achieve a quasi-stationary state for the reaction, which was confirmed by using sweep rates down to  $1 \text{ mV s}^{-1}$  and observing that the current potential profile was kept unaltered for the LBL chitosan–Pt electrode. The values of the current were normalized by the area of exposed platinum, which was calculated from the coulometric charge of hydrogen desorption by the geometric area ( $210 \mu\text{C cm}^{-2}$ ). Both electrodes reduce the oxygen, with the only difference that the plot for the Pt/chitosan/PVS electrode is shifted by approximately 130 mV. This drawback in that chitosan causes a delay in the oxygen reduction onset can be caused by slow diffusion of molecular oxygen to the available platinum sites inside the chitosan matrix. In spite of this delay in the oxygen reduction onset, the electroactivity observed indicates that LBL films of chitosan/PVS can be used as matrix to

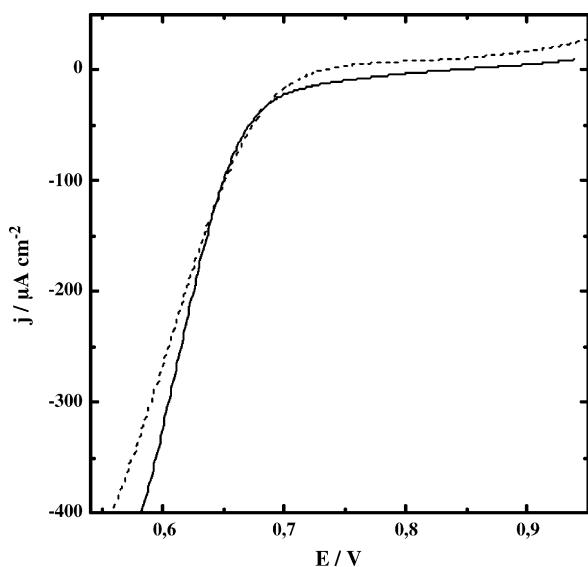


Fig. 4. Potential linear scanning for the LBL Pt/chitosan/PVS electrode (---) and the 10-bilayer LBL film of chitosan/PVS adsorbed on the Pt/chitosan/PVS electrode (—) in an aqueous solution of  $\text{HClO}_4$  (pH 2.0) with methanol ( $0.5 \text{ mol L}^{-1}$ ) under  $\text{O}_2$  flux;  $v = 10 \text{ mV s}^{-1}$ .

immobilize platinum in cathodes of micro DMFC and biofuel cells [24,25].

Fig. 4 shows the plots for the potential linear scanning of the LBL chitosan–Pt electrode (dotted line) and of another 10-bilayer LBL film of chitosan/PVS adsorbed on the Pt/chitosan/PVS electrode (full line) in an aqueous solution of  $\text{HClO}_4$  (pH 2.0) with methanol ( $0.5 \text{ mol L}^{-1}$ ), under oxygen flux. Note that the plot for the 10-bilayer LBL film of chitosan/PVS adsorbed on the Pt/chitosan/PVS electrode is slightly shifted to positive potentials in comparison with that of the Pt/chitosan/PVS electrode. The low permeability of the chitosan/PVS layers to methanol appears to increase the tolerance of the cathode to methanol.

#### 4. Conclusions

We have demonstrated that LBL films of chitosan serve as catalyst support for platinum particles. In spite of the delay in the ORR onset, the resulting LBL films with the metallic platinum were stable and electroactive. Moreover, the Pt/chitosan/PVS system allowed the diffusion/migration of  $\text{H}_3\text{O}^+$ , thus warranting the electrolytical connection of the electrochemical cell. Significantly, the low permeability to methanol may lead to a decrease in the crossover effect, and therefore the LBL films reported here are a viable alternative to thin films with Pt particles for the membrane-electrode assembly in a micro DMFC. In future works the control of architecture of the LBL technique and the biocompatibility of chitosan may be further exploited in bio fuel cells to be implanted in plants and animals. LBL films of chitosan may also be used in hybrid cells with a Nafion membrane, in which synergism is sought between the properties of Pt in self-assembled films and Nafion membranes.

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