

A Pt₃Sn/C Electrocatalyst Used as the Cathode and Anode in a Single Direct Ethanol Fuel Cell

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Abstract

This paper presents a study involving the use of Pt₃Sn/C electrocatalysts as cathodes and anodes in a single direct ethanol fuel cell. First, we studied the oxygen reduction reaction (ORR) using commercial Pt/C from ETEK and Pt₃Sn/C as electrocatalysts with an alloy degree of 92 %. The electrocatalytic activity of the material for oxygen reduction was assessed using the rotating disk electrode technique (RDE). When Pt₃Sn was tested for ORR in the presence of ethanol, the results showed greater tolerance to the cross-over effect than Pt/C in the electrochemical cell. The experiments in a single direct ethanol fuel cell showed that without oxygen pressurization of the cell, the maximum power density is higher using Pt₃Sn/C as both cathode and anode than using Pt₃Sn as an anode and Pt/C as a cathode. When using Pt₃Sn/C as both the cathode and anode in a direct ethanol fuel cell, cell performance enhances.

Keywords: Oxygen reduction reaction, DEFC, Polymeric precursor method

1. Introduction

Direct ethanol fuel cells (DEFCs) have received attention as the next alternative power source because of their high efficiency and their environmentally friendly characteristics (Heo, Shibata et al., 2008). Furthermore, ethanol is obtained from biomass and presents low toxicity (Andreadis & Tsiakaras, 2006; De Souza, Flausino et al., 2009). However, many problems still need to be solved, such as finding a more effective catalyst than Pt for the oxygen reduction reaction (ORR) and the cathodic half-cell reaction (Stamenkovic, Mun et al., 2007).

For the ethanol oxidation reaction, one of the best binary electrocatalysts described in the literature is the intermetallic alloy Pt₃Sn (Colmati, Antolini et al., 2005; De Souza, Parreira et al., 2010). Its high performance is

because the electronic interactions between Pt and the alloyed metals modify the lattice parameters of platinum, leading to a change in the electron density of the material by shrinking of the “d” band of platinum (electronic effect) (Tong, Kim et al., 2002; Alayoglu, Nilekar et al., 2008; Park, Lee et al., 2008).

The shrinking of the “d” band of platinum influences the ORR in that the kinetics of the ORR increase compared with pure Pt. This fact has been attributed to changes in the Pt-Pt bond distance, the number of Pt nearest neighbors, the electron density of states in the Pt 5d band and the nature and coverage of surface oxide layers (Min, Cho et al., 2000; Aricò, Shukla et al., 2001; Shukla, Neergat et al., 2001; Lima, Lizcano-Valbuena et al., 2006). This increase in kinetics occurs because the oxygen reduction activity increases with a decrease in the adsorption strength of the oxygenated species. The increase in activity is attributed to the strong electronic interaction between Pt and the non-noble metal, which reduces the reactivity of Pt with adsorbates (Lima, Lizcano-Valbuena et al., 2006).

Another problem that occurs in the cathode of DEFCs is the crossover effect. Crossover from the anode to the cathode in a direct liquid fuel cell (DLFC) has serious negative consequences for cell performance: it reduces the cell's coulombic and voltage efficiencies (Dillon, Srinivasan et al., 2004; Lopes, Antolini et al., 2008). In a DEFC, about 4 % of the ethanol is lost, which may be attributed to the crossover of ethanol from the anode to cathode (Zhu, Sun et al., 2009).

To overcome the ethanol crossover problem, a similar strategy to that used in the case of methanol (Hobson, Nakano et al., 2002; Dillon, Srinivasan et al., 2004) has been adopted, consisting of the development of membranes that are less permeable to ethanol. Despite these developments, completely preventing methanol crossover remains difficult. An alternative method to minimize this problem to an acceptable level is the selective development of electrocatalysts for the ORR that are tolerant of methanol (Oh & Kim, 2008). These materials have been widely studied in the literature (Drillet, Ee et al., 2002; Scott, Shukla et al., 2004; Baranton, Coutanceau et al., 2005; Yang, Coutanceau et al., 2005; Díaz & Zinola, 2007; Lee, Zhang et al., 2007; Oh, Lee et al., 2007; Jeyabharathi, Venkateshkumar et al., 2008; Oh & Kim, 2008; Zignani, Antolini et al., 2008), but so far, few studies have been devoted to the case of ethanol in DEFCs (Andreadis & Tsiakaras, 2006; Lopes, Antolini et al., 2008).

A recent work reported the use of a Pt₃Sn/C composite (obtained by the polymeric precursor method) as the anode catalyst for ethanol oxidation in a DEFC (De Souza, Parreira et al., 2010). In a comparative study, a DEFC using Pt₃Sn/C as the anode catalyst demonstrated improved performance compared with that of a PtSn/C ETEK, especially in the intrinsic resistance-controlled and mass-transfer regions. The better performance of the Pt₃Sn/C catalyst for ethanol oxidation was associated with a higher proportion of Pt₃Sn than in the commercial catalyst.

Considering the above points, this paper reports a study showing the use of a Pt₃Sn/C alloy produced by the polymeric precursor method (PPM) that was used as both the cathode and the anode of a DEFC. In the present study, a RDE was used to evaluate the relevance of the material for the ORR in the presence and absence of ethanol. The experiments using a direct ethanol fuel cell were performed with and without oxygen pressurization to observe the performance of the material (Pt₃Sn/C) as a cathode and anode compared with Pt₃Sn/C as an anode and Pt/C ETEK as a cathode.

2. Experimental

The electrocatalyst characterization has been described in a previous publication (De Souza, Parreira et al., 2010). The ORR measurements were conducted at room temperature ($T = 25\text{ }^{\circ}\text{C}$) using an Autolab PGSTAT 302N bi-potentiostat with a rotating disk electrode module. A glassy carbon (GC) disk (support for the working electrodes with 0.25 cm^2 of geometric area) was used as the working electrode. As counter electrode, a Pt foil (geometric area = 2 cm^2) was used, and an Ag/AgCl electrode and RHE were used as reference electrodes. The GC support was polished to a mirror finish with a 1 mm alumina suspension, there has been studies of electrode property being altered as a result of over polishing; care must be exercised. And it was washed in a water/ethanol mixture before each experiment. The water used in all experimental procedures was obtained from a Milli-Q system from Millipore[®].

The working electrodes in the electrochemical experiments were prepared using an ink made of carbon materials, prepared as proposed by Paulus *et al.* (Paulus, Schmidt et al., 2001) by dispersing 5 mg of the powder in 5 mL of water and mixing for 60 min in an ultrasonic bath. After that, 20 μL aliquots of the dispersion were pipetted onto the glassy carbon substrate of the disc. After the evaporation of the water in a nitrogen stream, 20 μL of a diluted Nafion[®] solution (5 wt.%, Fluka) were pipetted onto the electrode surface to attach the catalyst particles onto the glassy carbon. The ratio of H₂O/ Nafion[®] in the solution was approximately 100/1.

The CO-stripping experiments were carried out in a 0.5 mol L⁻¹ H₂SO₄ solution. A RHE and a Pt wire were used, respectively, as the reference electrode and the counter electrode. CV experiments were performed in a N₂ purged system. Then, CO was added to the cell and adsorbed at 0.2 V for 20 min. The excess CO was eliminated with N₂ gas for 20 min, keeping the electrode polarized. The stripping charges determined were between 0.05 V and 1.1 V, using a 10 mVs⁻¹ scan rate. The experiments were performed at room temperature.

In all single-cell tests, the catalyst loading was 20 wt.%. An alloy of Pt₃Sn/C prepared using the PPM was used as the anode catalyst, and the alloy Pt₃Sn/C PPM or Pt/C ETEK was used as the cathode in the gas diffusion electrodes. The diffusion layer consisted of carbon powder (Vulcan XC-72, Cabot) with 15 % (w/w) polytetrafluoroethylene (PTFE, TE-306A, DuPont) deposited onto a carbon cloth substrate. The electrocatalyst was deposited on top of this layer in the form of a homogeneous dispersion made with Nafion® solution (5 wt.%, Aldrich) and isopropanol (J.T. Baker). All electrodes contained 1 mg Pt cm⁻² in the anode or cathode. After preparation, the electrodes were hot pressed on both sides of a Nafion® 117 membrane at 125 °C for 2 min under a pressure of 225 kg cm⁻². Prior to use, the membranes were exposed to 3 wt.% H₂O₂, washed thoroughly with distilled water and treated with 0.5 mol L⁻¹ H₂SO₄. The performance of the ethanol fuel cell containing each catalyst was determined in a single cell with a geometric area of 5 cm². The temperature was set to 100 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel (2 mol L⁻¹ ethanol aqueous solution) was delivered at approximately 2 mL min⁻¹, and the oxygen flow was set to 500 mL min⁻¹. The oxygen pressures used were 1 bar (without pressurization) or 2 bar (with pressurization). Polarization curves were obtained using a TDI RBL 488 electronic load.

3. Results and Discussion

3.1 Physical Characterization of the Pt₃Sn/C electrocatalysts

Physical characterization was reported in a previous paper from our group (De Souza, Parreira et al., 2010). Briefly, using X-ray diffraction (XRD), the results indicated that 23 % (of a possible 25 %) of the Sn was alloyed with Pt, forming a dominant Pt₃Sn phase. Transmission electron microscopy (TEM) showed good dispersion of the electrocatalyst and small particle sizes (3.6 nm ± 1 nm). The findings indicated that the PPM approach can be used to produce almost exclusively Pt₃Sn/C (> 90 %) if the synthesis conditions are well controlled.

3.2 Electrochemical Experiments

Figure 1 presents the cyclic voltammograms of the electrocatalysts Pt/C ETEK and Pt₃Sn/C PPM in a 0.5 mol L⁻¹ H₂SO₄ aqueous solution. In this figure, observe that for all profiles, there were processes associated with hydrogen UPD adsorption and desorption between 0.05 and 0.4 V, as extensively discussed in prior literature (Spinacé, Neto et al., 2004; Liu, Mitsushima et al., 2006; Oh, Lee et al., 2007; De Souza, Flausino et al., 2009). In the case of Pt₃Sn/C PPM, some differences in the hydrogen UPD adsorption and desorption were noticed in comparison with Pt/C. In the case of Pt₃Sn/C PPM, broad and smaller hydrogen adsorption–desorption peaks were observed instead of the well-defined hydrogen characteristics for polycrystalline Pt in Pt/C, likely caused by structural modifications of Pt due to the Pt–Sn interaction discussed in the work of Kin et al. (Kim, Choi et al., 2008).

The electrocatalytic activity and kinetics of the oxygen reduction reaction on the Pt₃Sn/C PPM electrocatalysts were studied using RDE experiments at 3600 rpm in 1 mol L⁻¹ sulfuric acid aqueous solution saturated with oxygen in the oxygen reduction potential region, i.e., from 0.1 to 0.8 V at a scan rate of 10 mVs⁻¹. In Figure 2, a comparison of the polarization curves obtained for ORR on Pt₃Sn/C with Pt/C ETEK at a rotation rate of 3600 rpm is presented both with and without ethanol.

The results presented in Figure 2 clearly indicate that the electrocatalytic activity of Pt₃Sn/C PPM is similar to that of Pt/C ETEK, but with Pt showing higher activities for ORR until the region of limit diffusion mass current density. The mass current densities for ORR using Pt₃Sn/C were lower than those using Pt/C ETEK in all potential regions, except in the region of limit diffusion mass current density. In the region of limit diffusion mass current density at 0.5 V, the mass current density values were almost the same for ORR using Pt₃Sn/C as for the same process using Pt/C. This result is in agreement with that reported by Jeyabharathi et al. (Jeyabharathi, Venkateshkumar et al., 2008), who reported that PtSn/C materials had behavior similar to that of Pt/C. However, in that paper, Pt₃Sn/C materials were not used. Even though the effect for ORR is almost the same using Pt₃Sn/C and Pt/C ETEK, further studies described in this paper have shown that Pt₃Sn/C presents a higher electrocatalytic activity than Pt/C ETEK for ORR, using ethanol in the electrolyte. The effect observed for the material here highlights the value of Pt₃Sn/C PPM, which is derived from the electronic effects caused by changes in the platinum “d” band levels (Min, Cho et al., 2000; Aricò, Shukla et al., 2001; Shukla, Neergat et al., 2001; Lima, Lizcano-Valbuena et al., 2006).

The onset potentials for the ORR were similar for the two electrocatalysts (see Table I). The value of the onset potential for the ORR using Pt₃Sn/C PPM was clearly smaller than the value found using Pt/C ETEK as electrocatalyst.

Another important point of study before ethanol single-cell experiments was the ethanol tolerance of the electrocatalyst. Figure 2 shows a comparison of the polarization curves for ORR on the electrocatalysts in 0.5 M H₂SO₄ with O₂ saturation, with and without 0.1 mol L⁻¹ ethanol, obtained at a rotation rate of 3600 rpm. When the polarization curves for the ORR in ethanol-containing electrolytes were compared with those in pure 0.5 mol·L⁻¹ H₂SO₄ (see Figure 2), all catalysts presented decreased overpotentials for the ORR because of the simultaneous occurrence of oxygen reduction and ethanol oxidation (Lima, Lizcano-Valbuena et al., 2006).

In the presence of ethanol, a decrease in the diffusion limit mass current density due to competition between the ORR and the EOR (ethanol oxidation reaction) was observed for Pt/C ETEK. For Pt₃Sn/C PPM, the variation for the diffusion limit mass current density for the ORR was very small. Using Pt/C ETEK, the diffusion limit mass current density for the ORR was 20 % smaller than that using the same electrocatalyst without ethanol. These results can be explained because the strength of adsorption of both CO (Tong, Kim et al., 2002; Alayoglu, Nilekar et al., 2008; Park, Lee et al., 2008) and O₂ (Min, Cho et al., 2000; Aricò, Shukla et al., 2001; Shukla, Neergat et al., 2001; Lima, Lizcano-Valbuena et al., 2006) is reduced in Pt₃Sn alloy materials, thereby facilitating a release of the catalytic sites and increase of the kinetic reaction.

The onset potentials for the ORR with ethanol were shifted by more than 50 mV in the negative direction for both electrocatalysts. This shift was within the typical range for the ORR with methanol in the electrolyte (acid medium), which is between 200 and 300 mV (Yang, Coutanceau et al., 2005; Lima, Lizcano-Valbuena et al., 2006; Jeyabharathi, Venkateshkumar et al., 2008; Li, Huang et al., 2008). However, to the best of our knowledge, no papers in the literature report a study involving the ORR with ethanol in the electrolyte.

Figure 3 presents the mass current densities of the ORR in the mixed diffusion-kinetic controlled region for each electrocatalyst analyzed in the form of Koutecky–Levich (K-L) plots for different electrode rotation rates. The slope of the K–L plots is directly related to the number of electrons involved in the reaction, where a higher slope correlates to a lower number of electrons (Calegario, Lima et al., 2006; Lim, Lee et al., 2008). For Pt₃Sn/C PPM, the slope was close to the Pt/C ETEK electrode, a reference catalyst for the ORR, where the reaction proceeds through the transfer of 4 electrons. This result reveals the promise of this material not only for ethanol oxidation [6] but also for oxygen reduction and applications in DEFCs.

Considering the above results, the electrocatalysts Pt/C ETEK and Pt₃Sn/C PPM were used as cathodes in single direct ethanol fuel cells. The anodes in both cases were Pt₃Sn/C MPP electrocatalysts. In addition, we used 20 wt.% Pt/C ETEK as the cathode for comparison. The polarization curves and power density curves were drawn under two conditions, one without pressurizing the cathode, where the crossover effect is more pronounced, and another with pressurization of the cathode.

Figure 4 compares the CO stripping sweeps at 10 mV s⁻¹ and 25 °C for both materials. For these experiments, the second cycle was observed to be sure that the voltammetric response corresponds to that in pure base electrolyte, which shows that a single cycle is enough to completely remove the CO coverage. It was also observed that at the first cycle, the hydrogen features do not seem to reflect a blocking of Pt sites because of the presence of absorbed CO. A shift to lower potentials of the onset potential of the CO oxidation was seen for the Pt₃Sn/C compared with Pt-ETEK/C, although the current density is higher for the Pt-ETEK/C. The bi-functional mechanism seems to operate on the bi-metallic Pt₃Sn/C catalyst because of formation of oxygenated species onto Sn (Vigier, Coutanceau et al., 2004). In addition, the oxidation of CO absorbed occurs over a larger potential on Pt₃Sn/C compared to Pt-ETEK. This broadness can be explained because of the presence of CO_L (linearly-bonded CO) and CO_B (bridge-bonded CO) on Pt sites (Massong, Wang et al., 2001). The superior CO oxidation ability of Pt₃Sn/C was also observed by García-Rodríguez *et al.* (García-Rodríguez, Somodi et al., 2009), who explain it by Sn-oxygenated species formation and an electronic effect due to an enlargement of the Pt-Pt bond in the Pt₃Sn network and a downward shift of the d-band center after alloying with Sn. These results were also corroborated by Simões et al. (Simões, dos Anjos et al., 2007). They affirmed that the reaction mechanism of CO removal from the electrode surface, at low potential region, can occur because of the participation of Sn hydroxides, because in the bimetallic catalyst PtSn, CO binds only to Pt atoms and not to the Sn atoms, whereas OH has an energetic preference for the Sn sites.

Figure 5 presents both the polarization (a) and power density curves (b) in a direct ethanol fuel cell without pressurizing the cathode. In this figure, one can see the superiority of the electrocatalyst Pt₃Sn/C MPP over the catalysts Pt/C ETEK, with a full power density about 17 % higher. A possible reason is that the ORR is less

affected by the presence of ethanol (crossover), which indicates that the Pt₃Sn/C electrocatalyst is good not only for the ethanol oxidation reaction (De Souza et al., 2010) but also for the oxygen reduction reaction with and without ethanol in the electrolyte.

When the cathode was output pressurized to reduce the crossover and increase the kinetics of the ORR, the performance of the two catalysts was quite similar. Figure 6 shows the results for Pt₃Sn/C PMM used as both cathode and anode. The results for Pt₃Sn/C as anode and Pt/C ETEK as cathode can be seen in our previous publication (De Souza, Parreira et al., 2010), although the performance of the cell was better using Pt₃Sn/C PPM as both the cathode and anode.

On the basis of the above results, the Pt₃Sn/C PPM electrocatalyst can be used as a possible substitute for Pt/C as a cathode with or without output pressurization to provide performance similar to or better than Pt/C. Note that without pressurization and without using Pt₃Sn/C PPM as a cathode, the performance of the direct ethanol fuel cell was 17 % higher than using Pt/C ETEK as a cathode, showing a great advantage of this electrocatalyst as a material for direct ethanol fuel cells because of their tolerance to the fuel and electrocatalysis of both ethanol oxidation and oxygen reduction.

4. Conclusions

Using a Pt₃Sn/C electrocatalyst as the cathode in the studied electrochemical cell presented the same diffusion limit mass current density as Pt for the ORR, along with more ethanol tolerance. When used as the anode and cathode in a DEFC without cathode pressurization, the power density was 17 % higher than using Pt/C ETEK as a cathode, and similar power density curves were obtained with 2 bar cathode pressurization. Hence, Pt₃Sn/C is a promising catalyst as both the anode and cathode in DEFCs. Pt₃Sn is more effective in efficiently oxidizing ethanol by eliminating the adsorbed intermediates, thereby facilitating the adsorption kinetics of the reactions and decreasing the catalyst poisoning.

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Table 1. Onset potentials for oxygen reduction using the different electrocatalysts studied

Electrocatalyst	Onset Potential / V vs Ag/AgCl	
	Without Ethanol	With Ethanol
Pt/C E-Tek	0.66	0.61
Pt ₃ Sn/C PPM	0.61	0.56

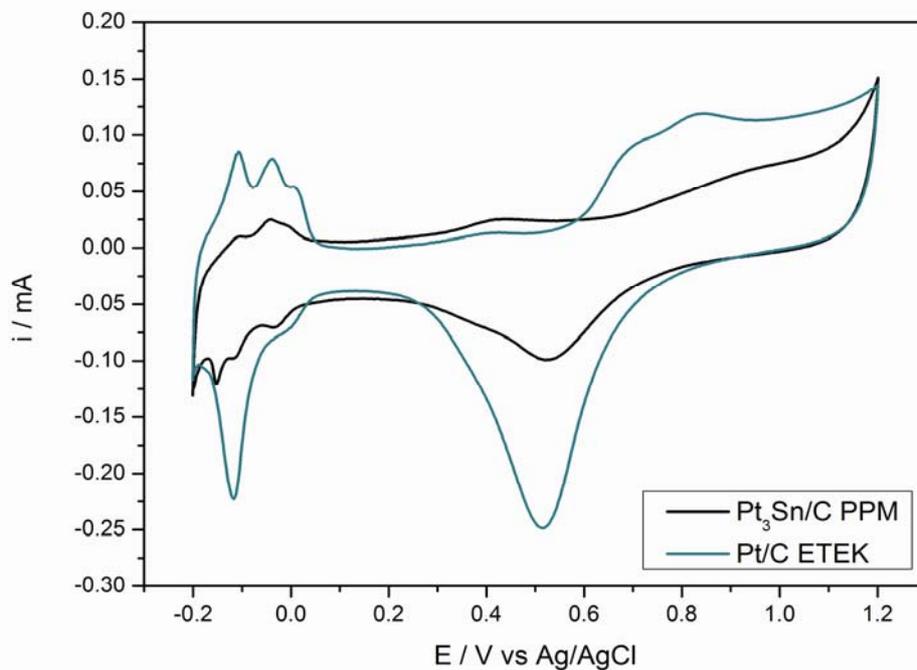


Figure 1. Cyclic voltammograms of Pt/C E-tek and Pt₃Sn/C in 0.5 mol L⁻¹ H₂SO₄, $\nu = 50 \text{ mV s}^{-1}$ and T = 25 °C

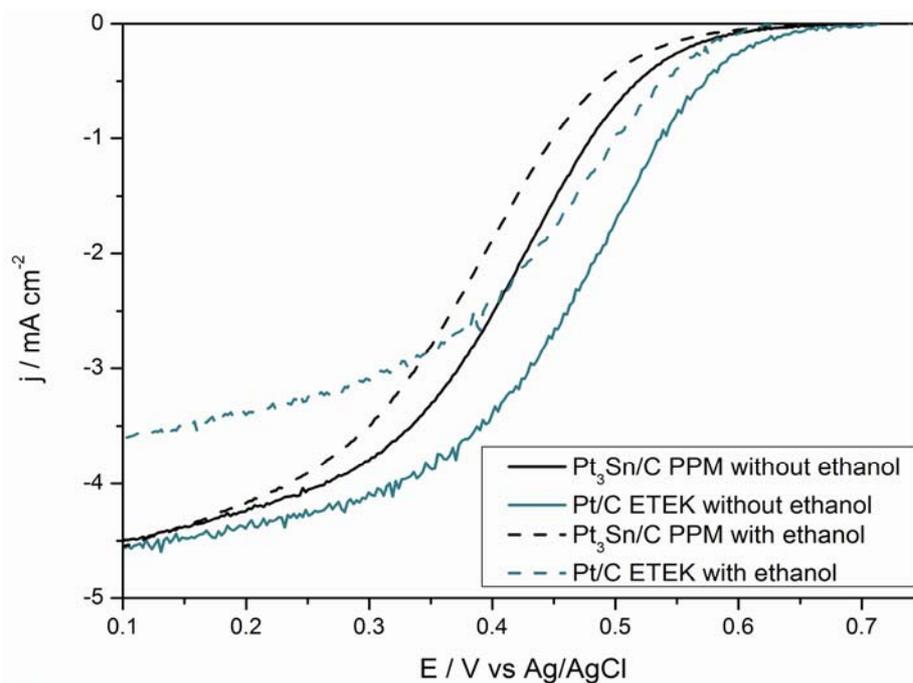


Figure 2. Polarization curves at steady state with and without 0.1 Mol L⁻¹ ethanol, $\omega = 3600 \text{ rpm}$. Polarization curves at steady state in 0.5 mol L⁻¹ H₂SO₄, $\omega = 3600 \text{ rpm}$

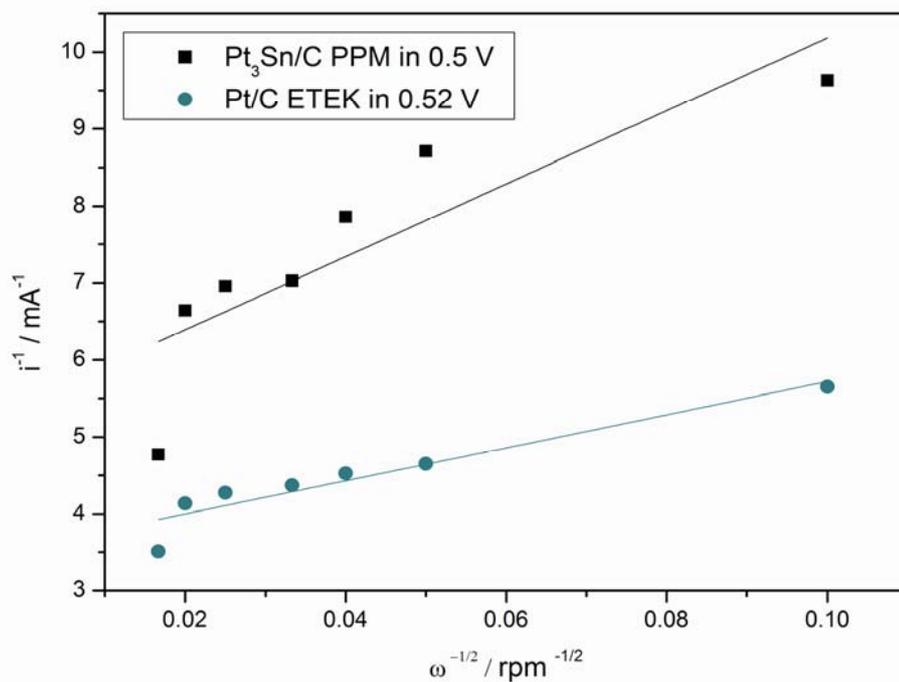


Figure 3. Koutecky-Levich diagram for ORR on the different electrocatalysts studied in H_2SO_4 0.5 mol L^{-1}

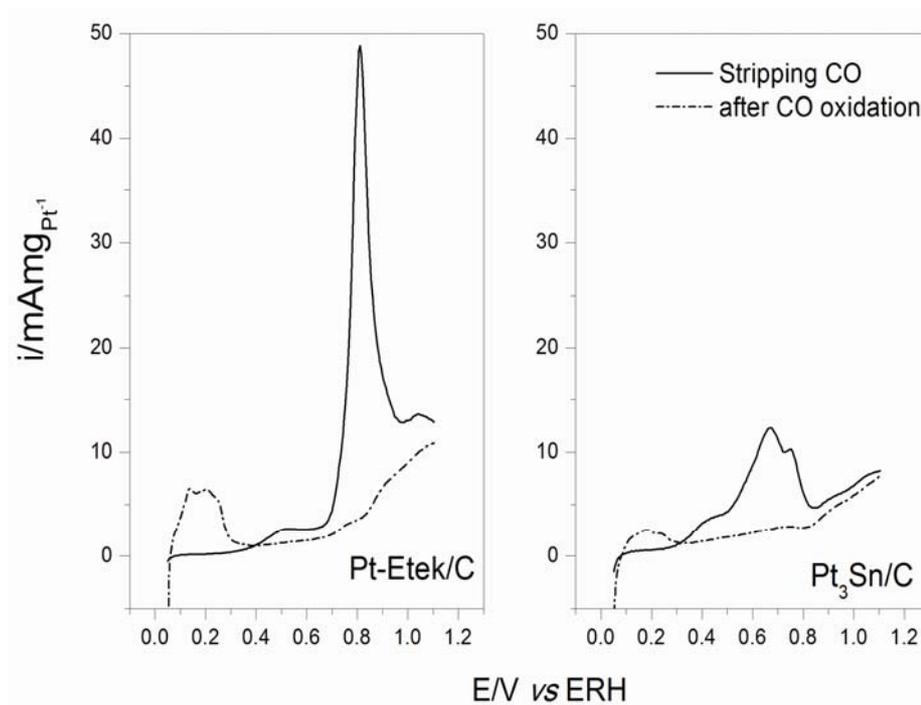


Figure 4. CO-stripping experiments on the two electrocatalysts studied

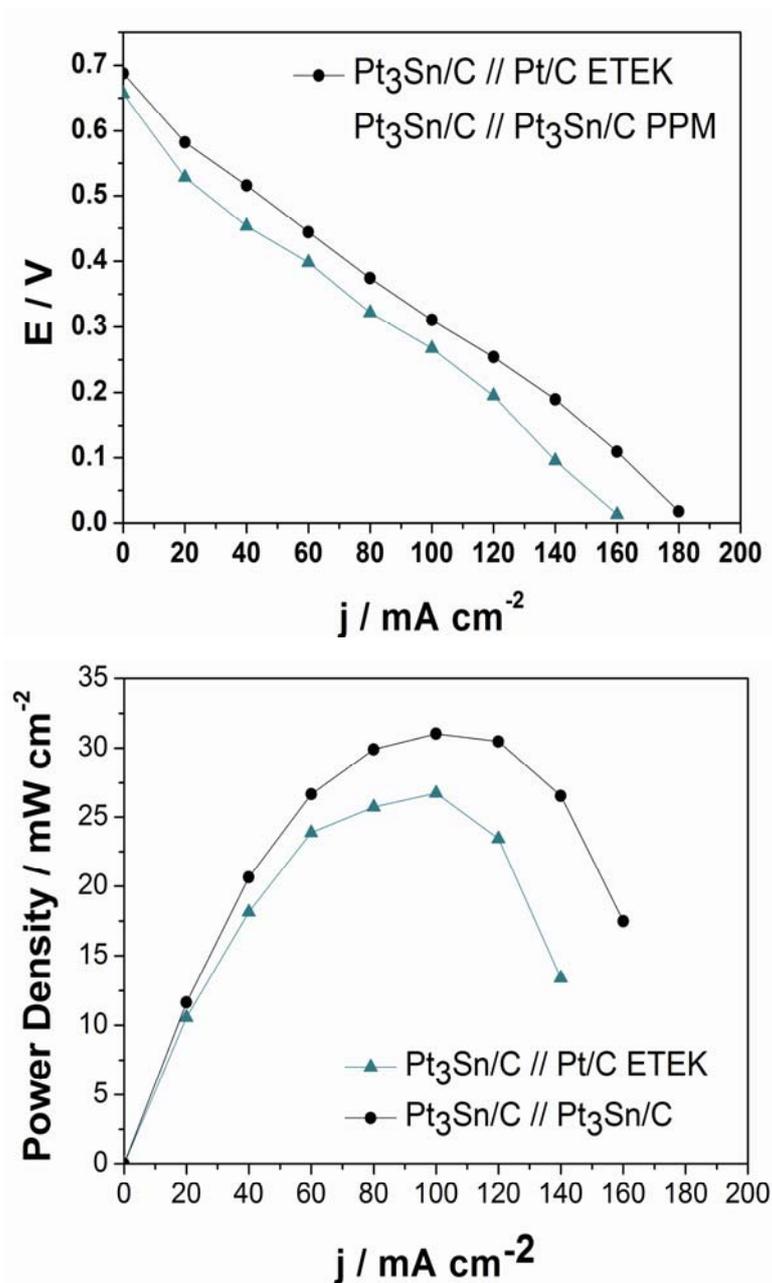


Figure 5. Polarization curves (a) and power density curves (b) in a 5 cm² DEFC at 100 °C using 20 wt.% Pt₃Sn/C PPM and Pt/C E-tek (1 mg Pt cm⁻²) as cathodes and Pt₃Sn/C (1 mg Pt cm⁻²) as the anode catalyst in both cases. Nafion[®] 117 was used as the membrane, and the ethanol concentration was 2 mol L⁻¹. There was no cathode pressurization

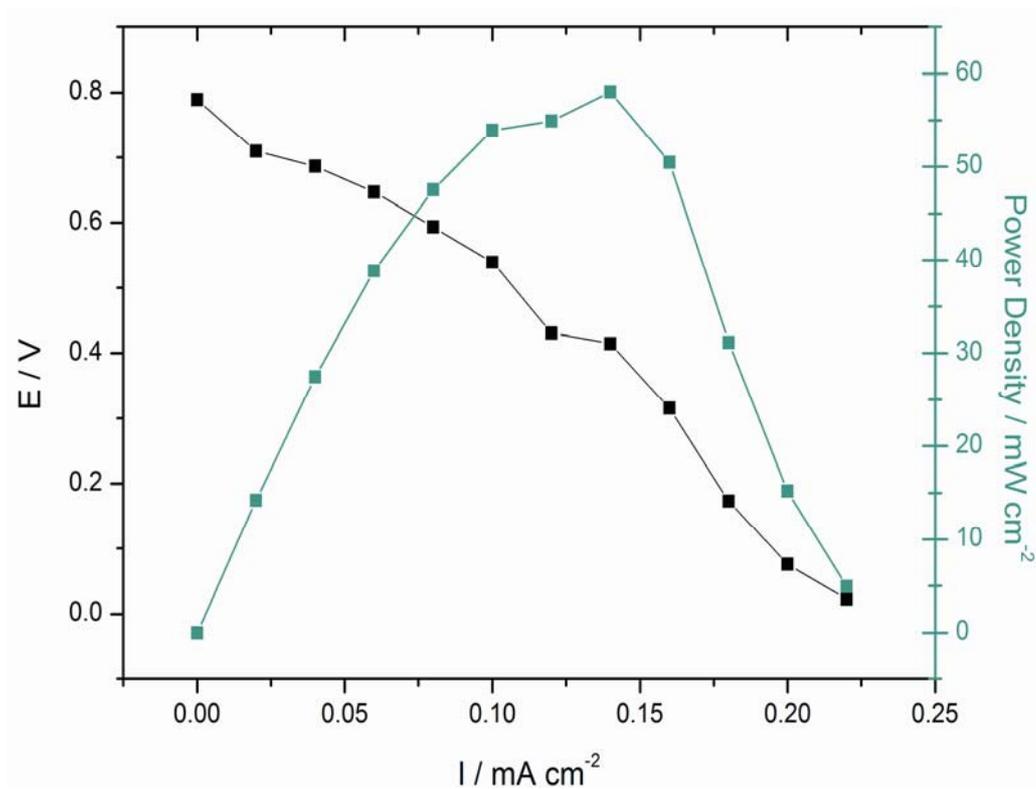


Figure 6. Polarization and power density curve in a 5 cm² DEFC at 100 °C using 20 wt.% Pt₃Sn/C PPM as both cathode and anode catalyst (1 mg Pt cm⁻²). Nafion[®] 117 was used as the membrane, and the ethanol concentration was 2 mol L⁻¹. O₂ pressure = 2 bar