Electrical performances and products distribution of a DEFC operating with Pt/C, $PtSn_{(alloy)}$/C and $PtSnO_2$/C as anode electrocatalysts

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Introduction

Direct Ethanol Fuel Cell (DEFC) is attractive as power sources for portable and mobile applications. Ethanol is an interesting fuel due to its high power density, non-toxicity and it is produced in large quantities from renewable sources. PtSn-based electrocatalysts have been shown the best results for ethanol electro-oxidation, however, the complete electro-oxidation of ethanol to CO_2 at low temperatures is difficult due to the breaking of the C-C bond and to the formation of intermediates that poison the platinum anode catalyst. Furthermore, studies have been shown that PtSn electrocatalysts where, Sn is reduced in the form of an alloy with Pt, as well, where Pt and SnO_2 phases coexist have shown good activities for ethanol electro-oxidation [1]. In this work, the electrical performances and the products distribution of a single DEFC were evaluated at 100°C using Pt/C, $PtSn_{(alloy)}$/C and $PtSnO_2$/C as anode electrocatalysts.

Experimental

$PtSnO_2$/C (20 wt% of metal loading and Pt:Sn molar ratio of 75:25) was prepared by an alcohol-reduction process [2]: $H_2PtCl_6.6H_2O$ and $SnCl_2.2H_2O$ were dissolved in ethylene glycol/water (3/1, v/v) and the Carbon Vulcan XC-72 was dispersed in this solution. The mixture was treated in an ultrasound bath for 20 min and then submitted to reflux for 3 h under open atmosphere. The obtained solid was filtered, washed with water and dried at 70°C for 2 h. The X-ray diffraction (XRD) patterns were performed with a Rigaku diffractometer model Multiflex II using a CuKα radiation source. The crystallite sizes were determined by the Scherrer equation. The Pt:Sn molar ratio was determined by the Energy Dispersive X-ray Spectroscopy (EDS) using a JEOL 6010LA operating at 20 kV. The membrane electrode assemblies (MEA) were prepared by hot pressing a pretreated Nafion 117 membrane placed between either a Pt/C, $PtSn_{(alloy)}$/C or a $PtSnO_2$/C anode (2 mg Pt cm^{-2} catalyst loading) and a 20 wt% Pt/C BASF cathode (2 mg Pt cm^{-2} catalyst loading) at 125°C for 10 min under a pressure of 247 kgf cm^{-2}. DEFC performances were determined using a single cell with an area of 5 cm^2 at 100°C. The fuel was 2 mol L^{-1} of ethanol solution delivered at 2 mL min^{-1} and the oxygen flow was regulated at 500 mL min^{-1} and pressure of 2 bar. Pt/C (lot# F0381022) and $PtSn_{(alloy)}$/C (Pt:Sn molar ratio of 75:25) (lot# F0930209) were purchased from BASF. The products distribution were determined by Gas Chromatography (GC) using a 7890A Agilent GCSystem with a HP/PlotU column and a TCD detector. The concentrations of the products were determined using calibration curves.

Results and Discussion

XRD patterns of the electrocatalysts are shown Figure 1a. Pt/C electrocatalyts showed the characteristic peaks of face-centered cubic (fcc) structure of Pt [2]. $PtSn_{(alloy)}$/C electrocatalyst also showed the Pt (fcc) peaks, however, they were shifted to small angles due to the presence of PtSn alloy. $PtSnO_2$/C electrocatalyst showed the Pt (fcc) peaks and the presence of SnO_2 tetragonal phase [2]. The Pt:Sn molar ratio of the $PtSnO_2$/C electrocatalyst determined by EDX was 80:20 and was similar to the nominal value. The crystallite size was

about 2 nm and it was similar to the observed for commercial Pt/C and $PtSn_{(alloy)}$/C electrocatalyts. The electrical performances of the electrocatalysts are shown in Figure 1b and Table 1. $PtSnO_2$/C electrocatalyst showed a superior performance (power density of 127 mW cm^{-2}) compared to $PtSn_{(alloy)}$/C (87 mW cm^{-2}) and Pt/C (24 mW cm^{-2}).

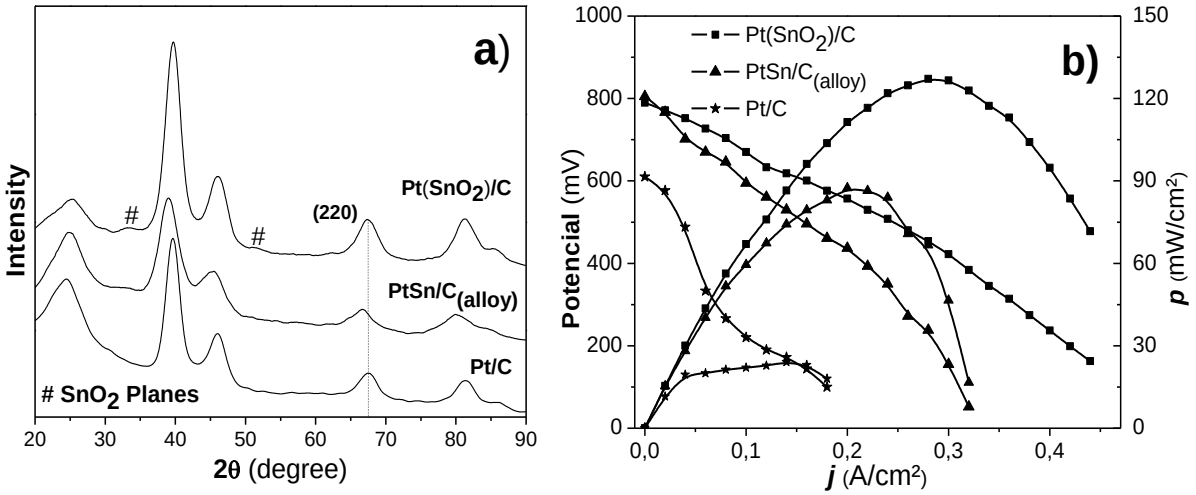

Figure 1: a) *XRD patterns and* ***b)*** *Electrical performances of the anodic electrocatalysts (100°C, oxygen pressure of 2 bar, ethanol concentration of 2 mol L^{-1} and flow ratio of 2 mL min^{-1})*

The products selectivity can be seen in Table 1. Pt/C and $PtSn_{(alloy)}$/C electrocatalysts were more selective to the formation of acetaldehyde (transference of 2 electrons per molecule de ethanol) while for $PtSnO_2$/C electrocatalyst an increase of acetic acid (transference of 4 electrons per molecule de ethanol) production was observed. Unfortunately, the formation of CO_2 was very small for all electrocatalysts.

Table 1: *Products selectivity, maximum current and power density values at 50 mV.*

Electrocatalyst	Selectivity (%)			j_{max} (mA cm^{-2})	p_{max} (mW cm^{-2})
	AAL*	AA*	CO_2		
Pt/C	90	5	5	200	24
$PtSn/C_{(alloy)}$	72	23	5	320	87
$Pt(SnO_2)/C$	54	44	3	440	127

*AAL: acetaldehyde, AA: acetic acid.

Conclusions

$PtSnO_2$/C electrocatalyst showed a superior electrical performance on a single DEFC operating at 100°C compared to commercial $PtSn_{(alloy)}$/C and Pt/C electrocatalysts. The superior performance of $PtSnO_2$/C electrocatalyst could be attributed to a further oxidation of acetaldehyde, formed from ethanol dehydrogenation, to acetic acid and/or to ethanol that could be directly oxidized to acetic acid on these sites.

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References

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