

PtSnCe/C and PtSnIr/C Electrocatalysts for Ethanol Oxidation: DEFC and FTIR “*in-situ*” studies

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The development of materials for ethanol oxidation reaction (EOR) is very important for improving the efficiency of direct ethanol fuel cells (DEFC). However, the complete electro-oxidation of the ethanol to CO₂ is a challenge for the effectiveness of catalysts. Pt is the most active metal to the oxidation of this alcohol and its electrocatalytic activity can be improved by the addition of some other metals such as Ir [1], Ce [2] and Sn [3]. This work presents a study of PtSnCe/C and PtSnIr/C electrocatalysts for ethanol oxidation reaction EOR. These materials were prepared using a modified polymeric precursor method (PPM) [2-3]. PtSnCe/C electrocatalysts in different mass ratios (72:23:5, 68:22:10 and 64:21:15) and PtSnIr (1:1:1) were compared with Pt/C E-TEK and PtSn/C E-TEK for EOR. All the catalysts were (20% w/w) on carbon XC-72. The performances on single direct ethanol fuel cells were also evaluated. The mechanism of EOR was studied using *in situ* FTIR spectroscopy. Transmission electron microscopy (TEM) showed that the particles ranged in size from approximately 2 to 5 nm to all PtSnCe/C proportions and 2 to 4 nm to PtSnIr/C. X-ray diffraction analysis indicated changes in the net parameters for Pt suggesting the incorporation of Sn and Ce into the Pt crystalline network with the formation of an alloy between Pt, Sn and/or Ce in PtSnCe/C. In PtSnIr/C X-ray diffraction analysis indicated metal Pt and Ir. SnO₂ was almost in the noise level, indicating the possible formation of an amorphous SnO₂ phase.

In DEFC tests 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 solutions) was delivered at approximately 2 mL min⁻¹, and the oxygen flow was set to 500 mL min⁻¹ and pressure of 2 bar. All electrodes contained 1 mg Pt cm⁻² in the anode and cathode, except PtSnIr (Pt+Ir = 1 mg cm⁻²). In all tests Pt/C E-TEK was used as cathode. The performances of a DEFC for all catalysts PtSnCe/C and PtSn/C E-TEK are shown in Figure 1a. Figure 1b are shown PtSnIr/C and PtSn/C E-TEK catalysts.

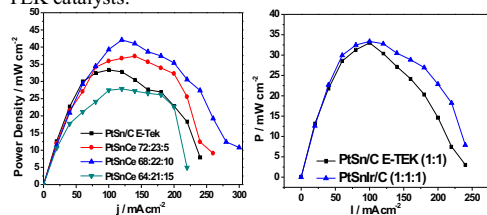


Figure 1. Power density curves in 5 cm² DEFC at 100 °C. Nafion[®] 117 was used as the membrane. 2 mol L⁻¹ ethanol with 2 mL s⁻¹ flux. (a) using all PtSnCe/C and (b) using PtSnIr/C.

The maximum power obtained using PtSnCe/C 68:22:10 (Figure 1a) was approximately 40% higher than the commercial material (44 mW cm⁻² vs. 32 mW cm⁻², respectively). The enhancement of activity for alcohol electro-oxidation resulting from the addition of CeO₂ to platinum catalysts was attributed by Qin and co-workers [4] to the bifunctional mechanism, where CeO₂ favors the formation of chemisorbed oxygen species.

The maximum power density obtained using PtSnIr/C (figure 1b) is slightly higher than commercial material with half content of platinum (31.5 mW cm⁻² vs 32 mW cm⁻², respectively). Promissory results have already been discussed in the literature using PtSn/C, PtIr/C and PtSnIr/C [1]. However, there are no works on the literature in which Ir can substitute half of the Pt content in the electrocatalyst.

In situ FTIR integrated bands intensities for acetic acid, acetaldehyde and CO₂ on PtSnCe/C 68:22:10, PtSnIr/C and PtSn/C E-TEK electrocatalyst, in 2 mol L⁻¹ CH₃COOH / 0.1 mol L⁻¹ HClO₄ solution are shown in Figure 2a, 2b and 2c respectively.

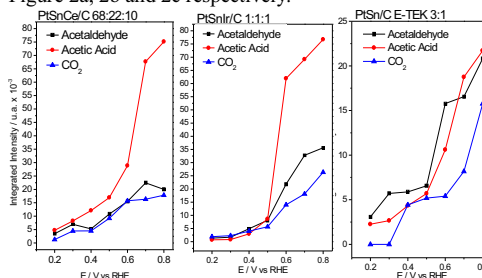


Fig.2: Integrated bands of spectra referent to main products of ethanol oxidation: acetaldehyde, acetic acid and CO₂.

The comparison of the band intensities shows that the production of acetic acid is favored for PtSnCe/C catalysts, while acetaldehyde and CO₂ are produced in the same proportion. Using PtSnIr/C catalyst is possible to observe that acetic acid and acetaldehyde production increases by increasing the electrode potential for the catalyst. The onset potential for acetic acid formation at 0.4 V, while the CO₂ production increases before 0.5 V. The acetaldehyde formation is bigger than CO₂ but it is smaller than acetic acid. On PtSn/C E-TEK acetic acid and acetaldehyde are produced in same amount and CO₂ is produced in small amount, but only slightly less than the other two products formed.

PtSnCe/C and PtSnIr/C electrocatalysts showed superior activity than the commercial PtSn/C material E-Tek for ethanol oxidation in a DEFC. For both materials acetic acid is the product formed in bigger proportion.

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