

Characterization of PtSn/C electrocatalysts prepared using citric acid as reducing agent for Direct Ethanol Fuel Cell (DEFC)

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1. Introduction

Fuel cells employing alcohols directly as combustible (Direct Alcohol Fuel Cell - DAFC) are attractive as power sources for mobile, stationary and portable applications. Compared to hydrogen-fed fuel cells, which need a reforming system or have problems of hydrogen storage, DAFCs use a liquid fuel, thus simplifying the fuel delivery system [1]. Ethanol offers an attractive alternative as a fuel because it is produced in large quantities from biomass and it is much less toxic than others alcohols. Due to the low electrocatalytic activity of platinum for practical DEFC (Direct Ethanol Fuel Cell) applications, elements like ruthenium and tin have been added to promote electroactivity. PtSn/C electrocatalysts have been described to be more active than PtRu/C electrocatalysts for ethanol electro-oxidation and their performances also depends greatly on preparation procedures and Pt:Sn atomic ratios [2]. In this work, PtSn/C electrocatalysts with Pt:Sn atomic ratios of 50:50 and 60:40 were prepared by CAM (Citric Acid Method) [3] using citric acid as reducing agent.

2. Experimental

The electrocatalysts were prepared with a metal loading of 20 wt. % using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich), $\text{SnCl}_2 \cdot x\text{H}_2\text{O}$ (Aldrich) as metals sources and Vulcan XC72R as carbon support. The electrocatalysts were characterized by energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). The electro-oxidation of ethanol was studied by cyclic voltammetry and chronoamperometry at room temperature in acid medium. The DEFC performances were determined in a single cell with an area of 5 cm^2 and $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$. The temperature was set to $90 \text{ }^\circ\text{C}$, the fuel was 2 mol L^{-1} ethanol solution delivered at approximately 1 mL min^{-1} and an oxygen flow of 500 mL min^{-1} and pressure of 2 bars was used.

3. Results and discussion

The EDX analysis showed that the Pt:Sn atomic ratios of the obtained electrocatalysts were similar to the nominal atomic ratios used in the preparation. The diffractograms of PtSn/C electrocatalysts showed four peaks at approximately $2\theta = 40^\circ$, 47° , 67° and 82° , which are associated with the (111), (200), (220) and (311) planes, respectively, of a face cubic-centered (fcc) structure characteristic of platinum and platinum alloys and two peaks at $2\theta = 34^\circ$ and 52° that were identified as a SnO_2 phase. The average particle sizes of PtSn/C electrocatalysts were estimated using the Scherrer equation and were in the range of 3 – 9 nm, as shown in Tab. 1.

On the electrochemical studies for ethanol oxidation, in the DEFC at $90 \text{ }^\circ\text{C}$, the $\text{Pt}_{50}\text{Sn}_{50}/\text{C}$ and $\text{Pt}_{60}\text{Sn}_{40}/\text{C}$ electrocatalysts prepared using citric acid as reducing agent, showed superior performance compared to commercial $\text{Pt}_{75}\text{Sn}_{25}/\text{C}$ E-TEK and Pt/C E-TEK (Fig. 1).

Table 1. Pt:Sn atomic ratio, mean particle sizes and maximum power density of the prepared electrocatalysts.

Catalyst	Nominal atomic ratio (%)	Atomic ratio EDX (%)	Crystallite size from XRD (nm)	Paricle size from TEM (nm)	Maximum power density (mW cm^{-2})
Pt ₅₀ Sn ₅₀ /C (CA)	(50:50)	(50:50)	8,5	4,8	32
Pt ₆₀ Sn ₄₀ /C (CA)	(60:40)	(62:38)	8,7	5,2	37
Pt ₇₅ Sn ₂₅ /C (E-TEK)	(75:25)	(70:30)	3,8	3,3	24
Pt/C (E-TEK)	-	-	3,7	-	7

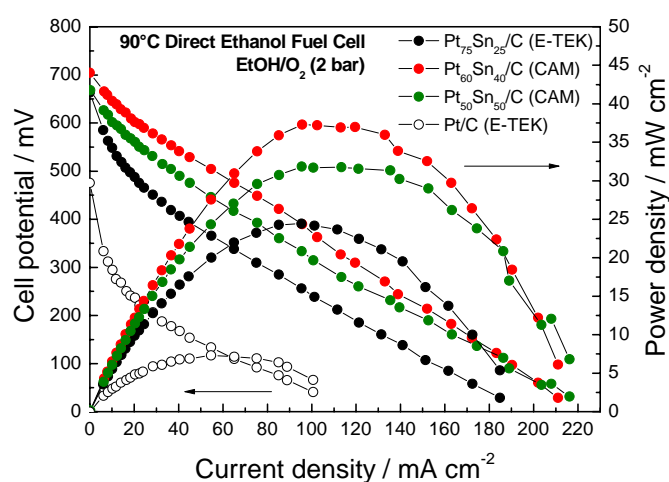


Figure 1. Polarization curves and power density curves in single DEFC with PtSn/C catalysts prepared by CAM and commercial Pt/C and Pt₇₅Sn₂₅/C by E-TEK.

4. Conclusions

The citric acid-reduction method (CAM) was found to be an effective method for making active PtSn/C electrocatalysts for ethanol oxidation. The X-ray diffractograms of electrocatalysts showed the typical fcc structure of platinum and platinum alloys with the presence of a SnO₂ phase. The presence of Sn oxide in the vicinity of Pt nanoparticles could offer oxygen species to remove the CO-like species of ethanolic residues on Pt active sites [4]. Pt₆₀Sn₄₀/C electrocatalyst showed higher power density than all electrocatalyst studied.

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