

Preparation of PtSn/C electrocatalysts using citric acid as reducing agent for direct ethanol fuel cell (DEFC)

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Abstract PtSn/C electrocatalysts (Pt:Sn atomic ratios of 50:50 and 60:40) were prepared using citric acid as reducing agent, and the pH of the reaction medium was varied by the addition of OH⁻ ions. The obtained electrocatalysts were characterized by energy dispersive X-ray analysis, X-ray diffraction, and transmission electron microscopy. The electrocatalysts were tested on the direct ethanol fuel cell (DEFC) at 90 °C. The obtained PtSn/C electrocatalysts showed the presence of a face-centered cubic, Pt, and SnO₂ phases. In DEFC studies, the PtSn/C electrocatalysts showed a superior performance compared to a commercial PtSn/C and Pt/C electrocatalysts from E-TEK.

Keywords Fuel cells

Introduction

The use of hydrogen in fuel cell technology has some limitations due to problems associated with production, purification, distribution, and principally storage. Consequently, the use of liquid fuels is of great interest, and methanol had been considered the most promising fuel because it is more efficiently oxidized than other alcohols; however, slow anode kinetics is observed, and it is considered as a toxic product. Thus, ethanol has been considered as a fuel alternative to methanol in low-temperature fuel cells because it is produced in large quantities from biomass and it is much less toxic. However,

its complete oxidation to CO₂ is more difficult than that of methanol due to the difficulties in C–C bond breaking and the formation of intermediates that poison the platinum anode catalysts [1–5].

Carbon-supported platinum is commonly used as anode catalyst in low-temperature fuel cells; however, pure Pt is not an efficient anodic catalyst for the direct ethanol fuel cell. Platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption of methanol and ethanol. Due to the low-electrocatalytic activity of platinum for practical direct alcohol fuel cell (DAFC) applications, elements like ruthenium and tin have been added to promote electroactivity [6, 7].

PtSn/C electrocatalysts have been described to be more active than PtRu/C electrocatalysts for ethanol electro-oxidation. Recently, Neto et al. [8] showed that PtSn/C electrocatalysts prepared by an alcohol-reduction process have a good performance for methanol and ethanol oxidation. The good performance was attributed to the fact that Pt adsorbs methanol or ethanol and dissociates C–H bonds, while SnO₂ species facilitates the oxidation of the intermediates formed on Pt sites. In this context, new preparation methods of PtSn/C electrocatalysts have been one of the topics studied on the electro-oxidation of alcohols.

Citric acid (CA) or sodium citrate has been used as reducing and/or stabilizing agent in the preparation of Pt-based electrocatalysts. Guo et al. [9] prepared a well-dispersed Pt/C electrocatalyst by the reduction of chloroplatinic acid with sodium borohydride and citric acid as a stabilizing agent in presence of ammonium hydroxide solution. The results indicated that the oxygen reduction reaction activity of the obtained catalyst was comparable to that of commercial Pt/C catalyst. Lin et al. [10] prepared Pt nanoparticles of average size of 2–3 nm using methanol as reducing agent and sodium citrate as stabilizer. Shimazaki

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Table 1 Pt:Sn atomic ratios and mean particle sizes of the PtSn/C electrocatalysts prepared using citric acid as reducing agent (20 wt.% metal loading, CA:PtSn molar ratio of 1:1, and OH⁻:PtSn molar ratio of 5:1)

Pt:Sn atomic ratio—nominal	Pt:Sn atomic ratio—EDX	Particle size—TEM (nm)	Crystallite size—XRD (nm)
50:50	50:50	4.8	8.5
60:40	62:38	5.2	8.7
75:25 E-TEK	70:30	3.3	3.7

et al. [11] prepared PtRu nanoparticles in aqueous media using citric acid as a capping agent and NaBH₄ as a reducing agent with the aid of pH control. The average size of the PtRu nanoparticles was about 2 nm, and the electrochemical measurement showed that the PtRu nanoparticles had catalytic activity for methanol. Guo et al. [12] prepared PtRu/C nanocatalysts by changing the molar ratio of citric acid to platinum and ruthenium metal salts and using sodium borohydride as a reducing agent. The obtained materials were tested as anode of a direct methanol fuel cell and showed a slightly higher performance than the commercial catalyst.

PtSn/C electrocatalysts with different Pt:Sn atomic ratios of 50:50, 60:40, 70:30, 80:20, and 90:10 were prepared using citric acid as reducing agent (CA:PtSn molar ratio of 1:1) [13]. The obtained materials showed the presence of metallic Pt with face-centered cubic (fcc) structure having average particles sizes in the range of 13–15 nm and a SnO₂ phase. The materials prepared with Pt:Sn molar ratios of 60:40 and 50:50 showed superior performance for ethanol electro-oxidation compared to the other ones. In this work, PtSn/C (60:40) and PtSn/C (50:50) electrocatalysts were prepared using citric acid as reducing agent, and the pH of the reaction medium was varied by the addition of OH⁻ ions. The obtained materials were tested for a direct ethanol fuel cell.

Experimental

PtSn/C electrocatalysts (20 wt.% metal loading and Pt:Sn atomic ratios of 50:50 and 60:40) were prepared in a single step using H₂PtCl₆·6H₂O (Aldrich) and SnCl₂·xH₂O (Aldrich) as metals sources and Vulcan XC72R as carbon support. The metal sources and the citric acid (CA:PtSn molar ratio of 1:1) were dissolved in 50 mL of water. After this, a solution of KOH 1 mol L⁻¹ (OH⁻:PtSn molar ratios of 0:1, 5:1, and 10:1) was added under stirring, and finally the carbon support (160 mg) was added to this solution. The resulting mixtures were treated in an ultrasound bath for 5 min and submitted to reflux for 3 h under open

atmosphere. Finally, the mixtures were filtered, and the obtained solids (electrocatalysts) were washed with water and dried at 70°C for 2 h.

The Pt:Sn atomic ratios were obtained by EDAX analysis using a scanning electron microscope Philips XL 30 with a 20 KeV electron beam and equipped with EDAX DX-4 microanalyzer.

The X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Miniflex II using Cu K α radiation source ($\lambda=0.15406$ nm). The diffractograms were recorded from $2\theta=20^\circ$ to 90° with a step size of 0.05° and a scan time of 2 s per step. The average particle sizes of PtSn/C electrocatalysts were estimated using the Scherrer equation [8].

Transmission electron microscopy (TEM) was carried out using a Carl Zeiss CEM 902 apparatus with a Proscan high-speed slow-scan CCD camera and digitalized (1,024×1,024 pixels, 8 bits) using the analysis software. The particle size distributions were determined by measuring the nanoparticles from micrographs using image tool software.

The membrane electrode assemblies were prepared by hot pressing a pretreated Nafion 117 membrane placed between either a PtSn/C (50:50), PtSn/C (60:40) prepared by citric acid, or PtSn/C E-TEK anode (1 mg Pt cm⁻² catalyst loading) and a 20 wt% Pt/C E-TEK cathode (1 mg Pt cm⁻² catalyst loading) at 125 °C for 2 min under a pressure of 225 kgf cm⁻². The direct ethanol fuel cell performances were determined in a single cell with an area of 5 cm². The temperature was set to 90 °C for the fuel cell and 80 °C for the oxygen humidifier. The fuel was 2 mol L⁻¹ of ethanol solution delivered at approximately 2 mL min⁻¹, and the oxygen flow was regulated at 500 mL min⁻¹ and pressure of 2 bar. Polarization curves were obtained by using a TDI RBL 488 electronic load.

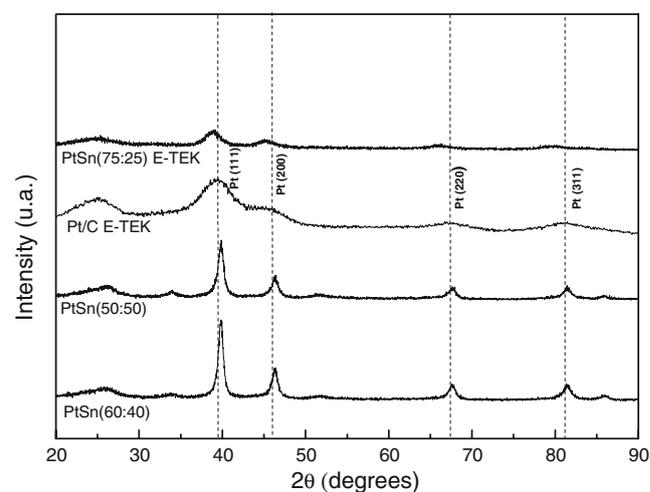


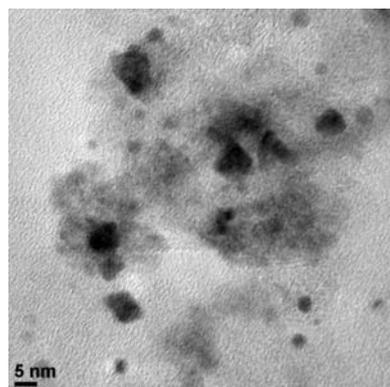
Fig. 1 X-ray diffractograms of Pt/C and PtSn/C electrocatalysts

Results and discussion

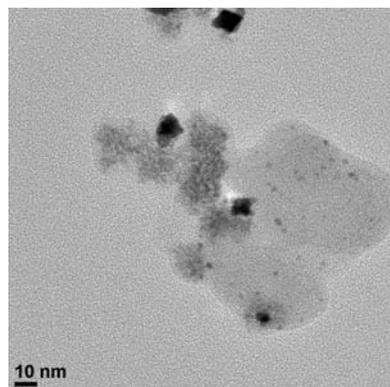
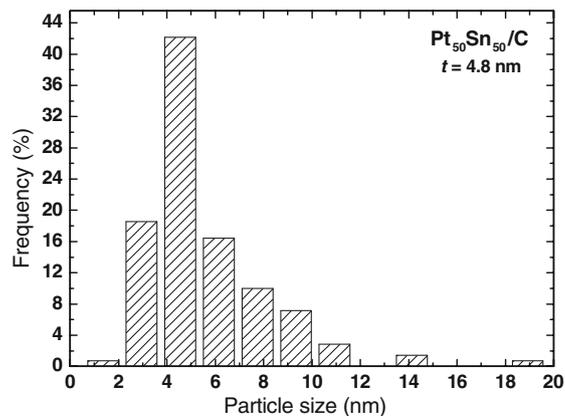
PtSn/C electrocatalysts were prepared using citric acid as reducing agent, and the pH of the reaction medium was varied by the addition of OH^- ions with the aim to decrease the crystallite sizes. It was observed in the preparation of Pt/C electrocatalysts that the OH^- ions could be adsorbed on the nanoparticles surface inhibiting their growth [14]. Initially, PtSn/C electrocatalysts with Pt:Sn atomic ratio of 50:50 were prepared by varying the OH^-/PtSn molar ratios of 0:1, 5:1, and 10:1. Without the addition of OH^- ions

(OH^-/PtSn molar ratio of 0:1), the pH of the reaction medium was 2, and the obtained material showed a mean Pt particle size of 13 nm. Pillai and Kamat [15] in the preparation of Ag nanoparticles using citrate as reducing agent also observed a growth of the nanocrystals. When PtSn/C electrocatalyst was prepared with OH^-/PtSn molar ratios of 5:1, the pH of the reaction medium increases to 5, and the obtained material showed a mean Pt particle size of 8.5 nm. The citric acid showed $\text{p}K_{a1}$ of 2.90, $\text{p}K_{a2}$ of 4.34, and $\text{p}K_{a3}$ of 5.66 [11]. Since the pH of the medium in this case was 5, the citric acid was found partly deprotonated.

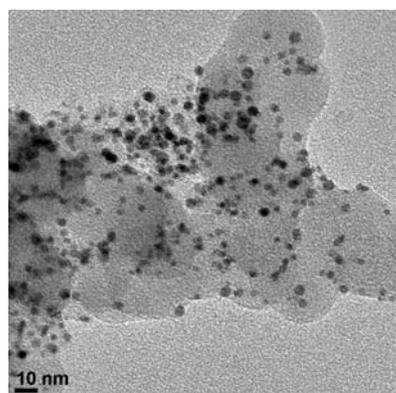
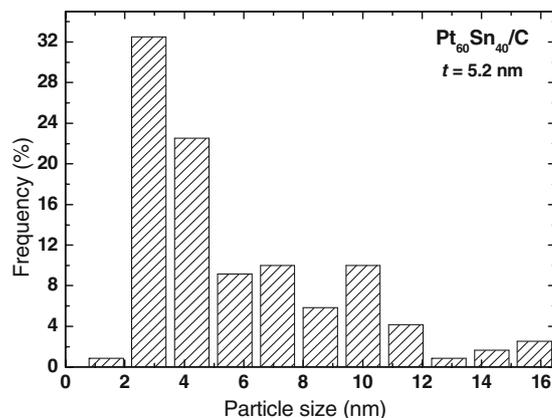
Fig. 2 TEM micrographs and particle size distribution of $\text{Pt}_{50}\text{Sn}_{50}/\text{C}$ (a), $\text{Pt}_{60}\text{Sn}_{40}/\text{C}$ (b), and PtSn/C (c) E-TEK electrocatalysts



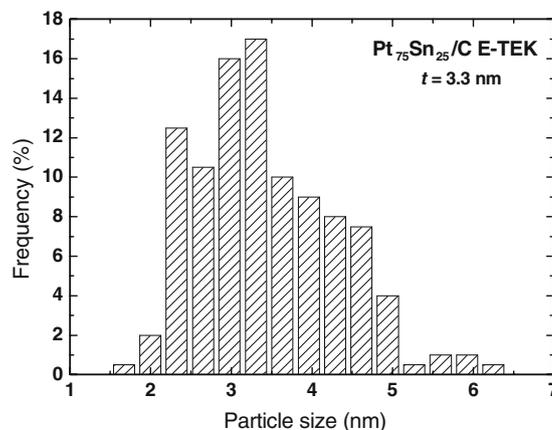
$\text{Pt}_{50}\text{Sn}_{50}/\text{C}$ (A)



$\text{Pt}_{60}\text{Sn}_{40}/\text{C}$ (B)



$\text{Pt}_{75}\text{Sn}_{25}/\text{C}$ (C)



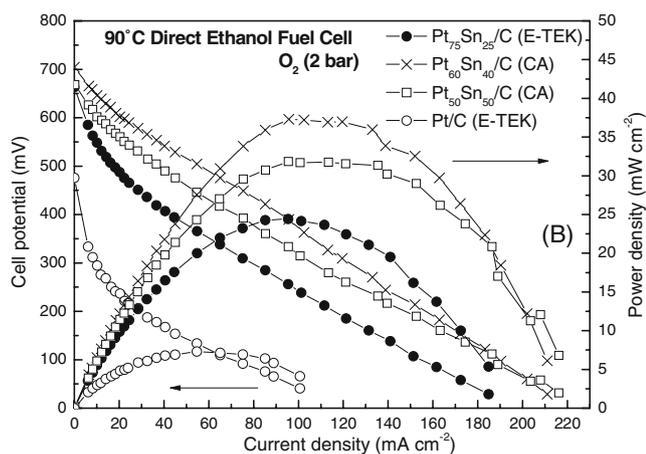


Fig. 3 Polarization curves and power density curves in single DEFC with PtSn/C catalysts prepared by CA and commercial Pt/C and PtSn/C by E-TEK as anode electrocatalysts for ethanol oxidation at 90 °C and 2 atm O₂ pressure using a 2 mol L⁻¹ ethanol solution. Anode metal loading 1 mg cm⁻². Cathode: 20 wt.% Pt/C, Pt loading 1 mg cm⁻²

Thus, the decrease of size was probably explained by the electrostatic repulsion induced by the deprotonated carboxyl group of citric acid adsorbed onto the surface of the nanoparticles [11]. When a OH⁻/PtSn molar ratio of 10:1 was used to prepare PtSn/C electrocatalyst, the pH of the reaction medium increases to 12. In this case, the deposition of metals on the carbon support was not observed. This could be explained by considering the zeta potential values of the carbon support and the metal nanoparticles. Increasing the pH of the reaction medium, both the metal nanoparticles and the carbon support become negatively charged, resulting thus in a repulsive force between the two, making it difficult to deposit metal nanoparticles on the carbon support [16, 17]. In this manner, PtSn/C electrocatalyst with Pt:Sn atomic ratios of 50:50 and 60:40 were prepared using OH⁻/PtSn molar ratio of 5:1 (Table 1). The energy dispersive X-ray analysis (EDX) analysis showed that the Pt:Sn atomic ratios obtained for both electrocatalysts were similar to the ones used in the preparations.

The X-ray diffractograms of the PtSn/C electrocatalysts are shown in Fig. 1. In all diffractograms, a broad peak at about 25° was associated with the Vulcan XC72R support material. The diffractograms of the PtSn/C electrocatalysts showed peaks at approximately $2\theta=40^\circ$, 47° , 67° , and 82° , which are associated with the (111), (200), (220), and (311) planes, respectively, of the fcc structure characteristic of platinum and platinum alloys. Also observed in the diffractograms were the two peaks at $2\theta=34^\circ$ and 52° that were identified as a SnO₂ phase [8]. The commercial PtSn/C electrocatalyst from E-TEK is a true PtSn alloy, and it was observed in the diffractogram only the peaks of Pt(fcc) phase shifted to lower angles in relation to Pt/C electrocatalyst. No peaks of SnO₂ phase were observed.

TEM micrographs of PtSn/C electrocatalysts (Fig. 2a and b) showed a large size distribution of the nanoparticles with an average size of 5 nm.

Figure 3 shows the performances of direct ethanol fuel cell (DEFC) using PtSn/C electrocatalysts prepared using CA and commercial Pt/C and PtSn/C electrocatalysts from E-TEK as anodes.

The DEFC results showed that the PtSn/C electrocatalysts prepared with Pt:Sn atomic ratio of 60:40 and 50:50 showed a superior performance compared to a commercial PtSn/C and Pt/C electrocatalysts from E-TEK. The superior performance could be attributed to the presence of SnO₂ species on the PtSn/C electrocatalysts prepared using CA [18]. Similar results were observed by Mann et al. [19] and Kowal et al. [20] using PtSnO₂/C electrocatalysts for ethanol electro-oxidation.

Conclusions

Active PtSn/C electrocatalysts for ethanol oxidation could be prepared using citric acid and OH⁻ ions as stabilizing agent. The obtained electrocatalyst showed the presence of a Pt(fcc) and SnO₂ phases. The SnO₂ species could react with water providing OH species to oxidize CO and/or intermediates oxygenated species that poison the Pt sites. Further work is now necessary to investigate and to elucidate the mechanism of ethanol electro-oxidation.

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