Ionics (2006) 12:309–313
DOI 10.1007/s11581-006-0053-z

ORIGINAL PAPER

Electro-oxidation of ethylene glycol on PtSn/C and PtSnNi/C electrocatalysts

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Received: 18 August 2006 / Revised: 4 October 2006 / Accepted: 6 October 2006 / Published online: 8 November 2006

Abstract A PtSn/C electrocatalyst with a Pt–Sn molar ratio of 50:50 and A PtSnNi/C electrocatalyst with a Pt–Sn–Ni molar ratio of 50:40:10 were prepared by alcohol-reduction process using ethylene glycol as solvent and reducing agent. The electrocatalysts were characterized by energy dispersive X-ray, X-ray diffraction, and cyclic voltammetry. The electro-oxidation of ethylene glycol was studied by cyclic voltammetry and chronoamperometry using the thin porous coating technique. PtSnNi/C electrocatalyst showed a superior performance compared to PtSn/C electrocatalysts in the potential range of interest for a direct ethylene glycol fuel cell.

Keywords PtSn/C · PtSnNi/C · Alcohol-reduction process · Electro-oxidation · Ethylene glycol · Fuel cell

Introduction

A direct alcohol fuel cell (DAFC) is a device in which the alcohol is fed directly into the fuel cell without any previous chemical modification and is oxidized at the anode, while oxygen is reduced to water at the cathode. Thus, DAFCs are very attractive as power sources for mobile and portable applications because it is not necessary to convert the fuel in a reformer into hydrogen. However, alcohols are very difficult to electro-oxidize completely, and up to now, methanol has been considered the most promising organic fuel because it is more efficiently oxidized than other alcohols. On the other hand, it is toxic and the methanol cross-over through the polymer-electrolyte membrane results in a decrease of efficiency [1–8]. Recently, Peled et al. [9, 10] reported that methanol/oxygen and ethylene glycol/oxygen fuel cells equipped with a new nanoporous proton-conducting membrane and using PtRu/C (Pt–Ru atomic ratio of 1:1) as anode catalyst provided a maximum power density of 400 and 300 mW/cm^2, respectively, which puts ethylene glycol in direct competition with methanol as a promising candidate for practical electric vehicles and stationary applications.

Kelaidopoulou et al. [11] observed that the addition of ruthenium, tin, or both onto platinum dispersed in polyaniline (PANI) increases the electro-oxidation of ethylene glycol in acid medium. The PANI/Pt–Sn assembly showed the highest electrocatalytic activity of the electrodes studied. However, the influence of PtSn composition was not investigated. We recently reported the electro-oxidation of ethylene glycol on PtRu/C and PtSn/C electrocatalysts with Pt–X (X=Ru or Sn) atomic ratios of 3:1, 1:1, and 1:3 [12]. Independent of the Pt–X atomic ratio used, PtSn/C electrocatalysts were better for ethylene glycol oxidation than PtRu/C electrocatalysts because the oxidation starts at lower potentials and high current values were obtained in the potential range for DAFCs (0.2–0.6 V) [12].

In this work, PtSn/C electrocatalyst with Pt–Sn atomic ratio of 50:50 and a new formulation of PtSnNi/C electrocatalyst with a Pt–Sn–Ni atomic ratio of 50:40:10 were prepared by alcohol-reduction process [13, 14] and tested for ethylene glycol oxidation using cyclic voltammetry and chronoamperometry.

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Experimental description

PtSn/C and PtSnNi/C electrocatalysts were prepared using $H_2PtCl_6{\cdot}6H_2O$ (Aldrich), $NiCl_2{\cdot}6H_2O$ (Aldrich), and $SnCl_2{\cdot}2H_2O$ (Aldrich) as metal sources, ethylene glycol (Merck) as solvent and reducing agent, and carbon Vulcan XC72R as support [13, 14]. The obtained solids were washed with deionized water several times until no chlorine ions could be detected in the wash water, using the silver nitrate test.

The Pt–Sn and Pt–Sn–Ni atomic ratios were obtained by energy dispersive spectroscopy (EDAX) analysis using a scanning electron microscope Philips XL30 with a 20-keV electron beam and provided with EDAX DX-4 microanalizer. The X-ray diffraction (XRD) analyses were performed using a Rigaku diffractometer model Multiflex with a CuKα radiation source.

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique [15, 16]. An amount of 20 mg of the eletrocatalyst was added to a solution of 50 ml of water containing three drops of a 6% polytetrafluoroethylene suspension. The resulting mixture was treated in an ultrasound bath for 10 min, filtered, and transferred to the cavity (0.30 mm deep and with and area of 0.36 cm^2) of the working electrode. The quantity of electrocatalyst in the working electrode was determined with a precision of 0.0001 g. In cyclic voltammetry and chronoamperometry experiments, the current values (I) were expressed in amperes and were normalized per gram of platinum (A/g_{Pt}). The quantity of platinum was calculated considering the mass of the electrocatalyst present in the working electrode multiplied by its percentage of platinum. The reference electrode was a reference hydrogen electrode and the counter electrode was a platinized Pt plate. Electrochemical measurements were made using a Microquimica (model MQPG01, Brazil) potentiostat/galvanostat coupled to a personal computer and using the Microquimica software. Cyclic voltammetry was performed in a 0.5-mol/l H_2SO_4 solution saturated with N_2. The evaluation of ethylene glycol oxidation was performed at 25 °C in three different concentrations: 0.1, 0.5, and 1.0 mol/l. For chronoamperometry, the electrolyte solution was 1 mol/l of ethylene glycol in 0.5 mol/l H_2SO_4.

Table 1 Pt–Sn and Pt–Sn–Ni atomic ratios and mean particle size of the prepared electrocatalysts

Electrocatalyst	Nominal atomic ratio			Atomic ratio-EDX			Particle size[a] (nm)
	Pt	Sn	Ni	Pt	Sn	Ni	
PtSn/C	50	50	–	52	48	–	2.0
PtSnNi/C	50	40	10	52	42	6	2.4

EDX energy dispersive X-ray

[a] Mean particle size calculated from X-ray diffraction data using Scherrer equation

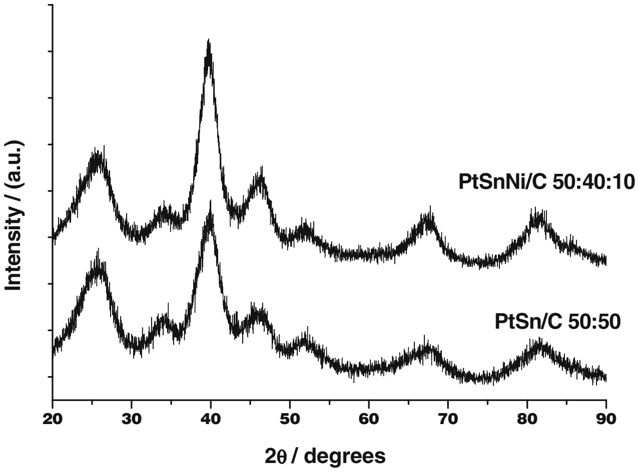

Fig. 1 X-ray diffractograms of PtSn/C and PtSnNi/C electrocatalysts

Results and discussion

The carbon-supported PtSn/C (Pt–Sn atomic ratio of 50:50) and PtSnNi/C (Pt–Sn–Ni atomic ratio of 50:40:10) electrocatalysts were prepared in a single step (coreduction of mixed ions), using ethylene glycol as solvent and reducing agent in the presence of carbon Vulcan XC72R [12–14]. The Pt–Sn and Pt–Sn–Ni atomic ratios of the obtained electrocalysts were similar to the nominal atomic ratios (Table 1). Attempts to prepare Pt–Sn–Ni compositions with more nickel content using this methodology failed. The X-ray diffractograms of the electrocatalysts are shown in Fig. 1. The PtSn/C electrocatalyst showed four diffraction peaks at about 2θ=40, 47, 67, and 82°, which are associated with the (111), (200), (220), and (311) planes, respectively, of the fcc structure characteristic of platinum

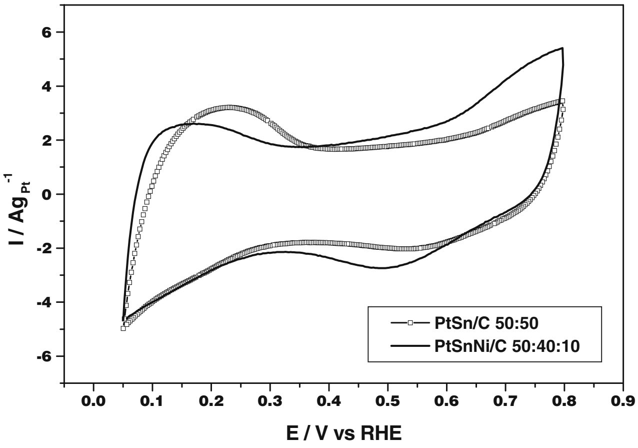

Fig. 2 CV of PtSn/C and PtSnNi/C electrocatalysts in 0.5 mol/l H_2SO_4 with a sweep rate of 10 mV/s

and platinum alloys [16]. The broad peak at about 25° was associated with the Vulcan XC72R support material. Two other peaks were also observed on the diffractogram at about 2θ=34 and 52° that were characteristic of cassiterite SnO_2 phase [17]. Xin and coworkers [18, 19] prepared PtSn/C electrocatalysts by a similar procedure using ethylene glycol as reducing agent. The analysis of the diffractograms also revealed the typical peaks relative to the fcc structure of platinum alloy. However, no peaks of SnO_2 phase were observed. This is probably because the electrocatalysts were prepared using pure ethylene glycol under argon flow, while in this work, the electrocatalysts were prepared using ethylene glycol/water at open atmosphere. Recently, Xin and coworkers [20] described the preparation of SnO_2 nanoparticles by heating ethylene glycol/water solutions containing $SnCl_2$. The diffractogram of PtSnNi/C electrocatalyst also shows the characteristic peaks of the Pt fcc structure and the presence of SnO_2 phase, like that observed for the PtSn/C electrocatalyst. However, no diffraction peaks indicating Ni or NiO phases were observed [21]. The mean particle sizes of PtSn/C and PtSnNi/C electrocatalysts were calculated from the angular position of the (220) peaks of fcc Pt structure using Scherrer equation [22] and were in the range of 2.0–2.5 nm (Table 1).

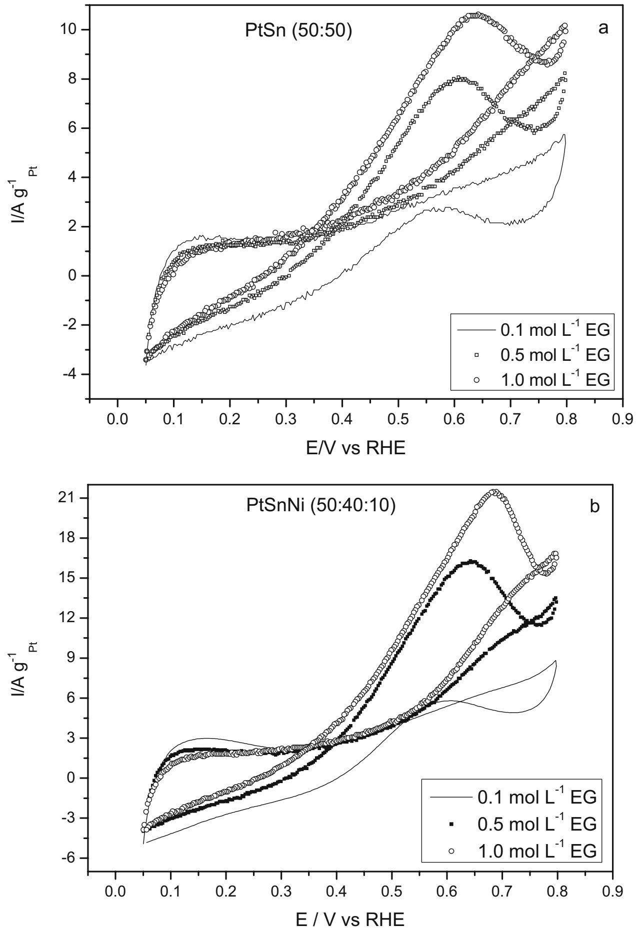

Fig. 3 CV of PtSn/C (**a**) and PtSnNi/C (**b**) electrocatalysts in 0.5 mol/l H_2SO_4, containing different concentrations of ethylene glycol with a sweep rate of 10 mV/s

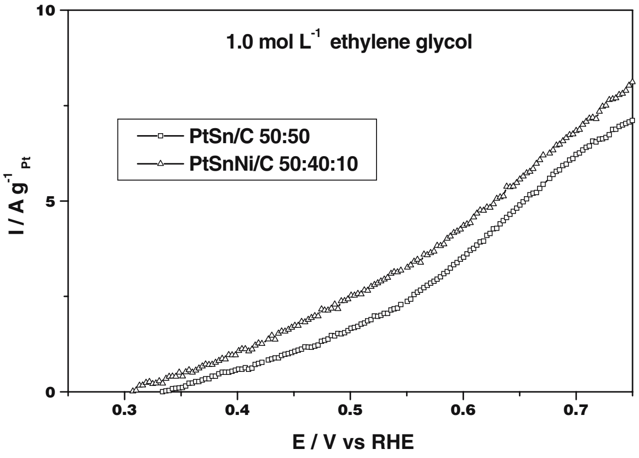

Fig. 4 CV of PtSn/C and PtSnNi/C electrocatalysts in 0.5 mol/l H_2SO_4, containing 1.0 mol/l of ethylene glycol with a sweep rate of 10 mV/s, considering only the anodic sweep

The cyclic voltammograms (CV) of PtSn/C and PtSnNi/C electrocatalysts in the absence of ethylene glycol are shown in Fig. 2. In this case, all CV do not have a well-defined hydrogen adsorption-desorption region (0.05–0.4 V), which is characteristic of platinum alloys [23–25]. The CV of PtSnNi/C electrocatalyst showed higher current values in the double layer region (0.4–0.8 V) than the PtSn/C electrocatalyst (50:50), which is probably due to the presence of tin and nickel oxide species [23–25]. Sung and coworkers [26, 27] prepared nonsupported PtRu (50:50) and PtRuNi (50:40:10) nanoparticles by a conventional reduction with $NaBH_4$. The XRD analysis showed the characteristic peaks of platinum fcc

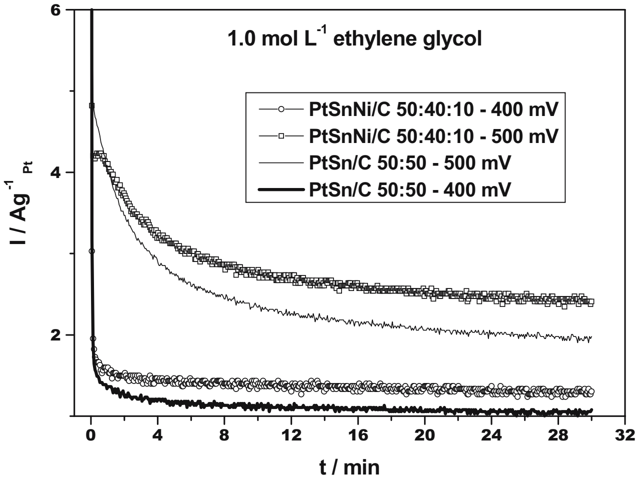

Fig. 5 Current–time curves at 0.4 and 0.5 V in 1 mol/l ethylene glycol solution in 0.5 mol/l H_2SO_4 for PtSn/C 50:50 and PtSnNi/C 50:40:10 electrocatalysts

structure and no peaks of fcc nickel and hcp ruthenium metals or oxides/hydroxides were observed. However, the X-ray photoelectron spectroscopy analysis revealed that about 40% of the ruthenium species were founded as ruthenium oxides and 85% of nickel species were founded as NiO, $Ni(OH)_2$, and NiOOH [26, 27].

The electro-oxidation of ethylene glycol was studied varying the concentration from 0.1 to 1.0 mol/l (Fig. 3). In a general manner, for PtSn/C and PtSnNi/C electrocatalysts, the current values in the hydrogen region (0.05–0.4 V) decrease with the increase of ethylene glycol concentration probably due to the increase of ethylene glycol adsorption on the surface [14]. For potentials more positive than 0.5 V, the current values increase with ethylene glycol concentration, even for 1.0 mol/l.

The PtSn/C and PtSnNi/C electrocatalysts performances in 1.0 mol/l of ethylene glycol are shown in Fig. 4. The anodic cyclic voltammetry responses were plotted after subtracting the backgrounds currents and current values were normalized per gram of platinum, considering that ethylene glycol adsorption and dehydrogenation occur only on platinum sites at ambient temperature [28–31]. The electro-oxidation of ethylene glycol started at approximately 0.35 V for PtSn/C electrocatalysts, while the substitution of a small amount of tin by nickel on the PtSnNi/C electrocatalyst decreased the onset potential to approximately 0.30 V and increased the current values in all ranges of the potential. The superior performance of the PtSnNi/C electrocatalyst was also confirmed by chronoamperometry measurements (Fig. 5). In all current-time curves, there is an initial current drop in the first 5 min followed by a slower decay, but the current values obtained for PtSnNi/C electrocatalyst were always higher than those obtained for PtSn/C (50:50) electrocatalyst. After chronoamperometry experiments, qualitative tests using dimethylglyoxime indicated no dissolution of nickel(II) ions in the solution [32].

Sung and coworkers [26, 27] also observed a superior activity of nonsupported PtRuNi (50:40:10) for methanol oxidation compared to PtRu (50:50) catalyst. The superior activity of the PtRuNi electrocatalyst was attributed to the modification of electronic properties of platinum and to the presence of nickel oxide species resulting in a combination of electronic effect and bifunctional mechanism [26, 27]. Recently, Dumesic and coworkers [33] reported the aqueous-phase reforming of oxygenated hydrocarbons, like glycerol and ethylene glycol, at temperatures near 500 K using nonprecious metal catalysts. They observed that the addition of Sn to Raney-Ni catalysts facilitated C–C bond cleavage and promoted the removal of adsorbed CO species by water–gas shift reaction, which increased the selectivity for hydrogen production.

Conclusions

The alcohol-reduction process was found to be an effective method for making active PtSn/C and PtSnNi/C (50:40:10) electrocatalysts for ethylene glycol direct oxidation. The X-ray diffractograms of electrocatalysts showed the typical fcc structure of platinum and platinum alloys with the presence of a cassiterite SnO_2 phase. PtSnNi/C electrocatalyst showed higher current values than PtSn/C electrocatalyst in the potential range of interest for a direct ethylene glycol fuel cell (0.20–0.60 V). Further work is necessary to modify our catalyst preparation methodology or prepare PtSnNi/C electrocatalyst by other methodologies in order to obtain and evaluate different Pt–Sn–Ni compositions. It is also necessary to conduct tests of these electrocatalysts in a single direct ethylene glycol fuel cell.

Acknowledgements The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo-FAPESP and Conselho Nacional de Desenvolvimento Científico e Tecnológico for financial support.

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