Short communication

Evaluation of Pt–Ru–Ni and Pt–Sn–Ni catalysts as anodes in direct ethanol fuel cells

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Abstract

In this study, the electrooxidation of ethanol on carbon supported Pt–Ru–Ni and Pt–Sn–Ni catalysts is electrochemically studied through cyclic voltammetry at $50\,^{\circ}C$ in direct ethanol fuel cells. All electrocatalysts are prepared using the ethylene glycol-reduction process and are chemically characterized by energy-dispersive X-ray analysis (EDX). For fuel cell evaluation, electrodes are prepared by the transfer-decal method. Nickel addition to the anode improves DEFC performance. When $Pt_{75}Ru_{15}Ni_{10}/C$ is used as an anode catalyst, the current density obtained in the fuel cell is greater than that of all other investigated catalysts. Tri-metallic catalytic mixtures have a higher performance relative to bi-metallic catalysts. These results are in agreement with CV results that display greater activity for PtRuNi at higher potentials.
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1. Introduction

The development of direct ethanol fuel cells (DEFCs) is a promising technology for power supply in mobile applications. The use of ethanol in fuel cells is attractive because it can be easily handled, has a low toxicity profile and can be produced in different countries from their agricultural products [1–4]; as a result, investigation into DEFCs is a fundamental topic for alternative energy sources. To date, different features of these devices have been investigated, such as the suitable electrolytic membrane and the appropriate anodic and cathodic electrocatalysts [5,6].

Numerous investigations suggest different anode catalytic mixtures for ethanol electrooxidation. Among them, Pt–Ru, Pt–Sn and Pt–Ru–Sn combinations have been studied extensively [7–14], however, few investigations with electrocatalytic mixtures such as Pt–Ru–Ni and Pt–Sn–Ni exist in the literatures [15–17]. In the nickel case, a direct comparison among all these mentioned electrocatalysts under similar experimental and evaluation conditions in DEFCs has not been performed. In this study, we conduct a direct experimental and evaluation comparison of Pt–Ru, Pt–Sn, Pt–Ru–Sn, Pt–Ru–Ni and Pt–Sn–Ni electrocatalytic mixtures to determine the most suitable catalytic mixture and test the effect of adding nickel to DEFC anodes in the performance of fuel cells.

2. Experimental

2.1. Electrocatalyst preparation

All electrocatalysts were prepared using the alcohol reduction process. In this process, ethylene glycol was used as a solvent and reduction agent. Vulcan Carbon® XC-72 was used as a support for all electrocatalysts [18]. The electrocatalytic mixtures and atomic ratios with a metal load of 20 wt.% were Pt:Ru (85:15 and 75:25), Pt:Sn (85:15 and 75:25), Pt:Ru:Sn (75:15:10 and 75:10:15), Pt:Ru:Ni (75:15:10 and 75:10:15) and Pt:Sn:Ni (75:15:10 and 75:10:15).

In the electrocatalyst preparation, the chemical precursors were $H_2PtCl_6\cdot6H_2O$ (Merck), $RuCl_3\cdot3H_2O$ (Merck), $SnCl_4\cdot5H_2O$ (Erbo) and $NiCl_2$ (Erbo). All solutions for the alcohol reduction process were prepared with 75/25 (v/v) ethylene glycol/water ratio. For each electrocatalytic mixture, the precur-

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sor solutions were ultrasonically scattered for 30 min. After, the pH value was adjusted to 11.7. The metal reduction process was conducted at 140 °C for 3 h. All mixtures were filtered for 2 h and dried at 70 °C for 2 h.

Catalyst inks were prepared by mixing the carbon supported catalyst powder with glycerol and a 5% Nafion suspension to form a 5:2 catalyst:Nafion® weight ratio [19,20] and 1.0 M tetra-butylammonium hydroxide (TBAOH) with overnight stirring to form homogeneous ink. The electrocatalytic ink was supported at the top of a vitreous carbon rod (the working electrode) to conduct an evaluation by cyclic voltammetry (CV). The covered electrocatalyst area in the working electrode was geometrically determined using an optical microscope and the area-values ranged between 0.22 and 0.36 cm^2.

2.2. Micro-chemical characterization

The micro-chemical characterization was made by energy-dispersive X-ray analysis (EDX) for atomic ratio determination. After the ethylene glycol-reduction process, this micro-chemical analysis was made for each electrocatalytic mixture and compared with a nominal atomic ratio. The EDX analysis was performed for a 3600 μm^2 electrocatalyst area in an analyzer associated with a scanning electron microscope (SEM) JEOL JSM-5910LV. Incident electron beam energies from 3 to 30 keV were used. In all cases, the beam was at normal incidence relative to the sample surface.

2.3. Electrochemical characterization

In cyclic voltammetry experiments, a typical three-electrode system with a pure-platinum-wire counter electrode was used. The reference electrode was the Ag/AgCl (3.0 M) system. However, all values are reported with respect to the normal hydrogen electrode (NHE). The working electrode was the transferred catalytic ink over the vitreous carbon rod.

An electrochemical characterization was performed in a Bio Analytical System® (B.A.S. 100 b/w) work station coupled to a personal computer. For each CV, N$_2$ (99.998% pure) was circulated for 5 min to remove the oxygen in the electrolyte. The nitrogen atmosphere was preserved during each test. The experiments were conducted in 1.0 M ethanol solutions in 0.5 M H$_2$SO$_4$ at 50 °C. The scan range was from −13 to 807 mV versus NHE and the scan rate was 50 mV s^{-1}.

2.4. Membrane electrode assemblies preparation and single fuel cells evaluation

After catalytic powder EDX analysis and ink elaboration, each catalytic mixture was brush painted onto a decal surface of fiberglass coated with Teflon®. The decal was heated in an oven at 140 °C for 30 min. The process of painting and heating was repeated until a catalysts loading of 2.0 mg cm^{-2} was reached in the anode and 1.0 mg cm^{-2} in the cathode (Pt E-Tek). The catalyst layer formed on the decal was hot pressed onto a Nafion® 117 membrane (sodium form) at 150 °C and 800 kg cm^{-2} for five minutes to produce the membrane elec-

Table 1
Fuel cell experimental conditions

Parameter	Values
Temperature	80 ± 1 °C
Ethanol flow	2.0 ± 0.1 ml min^{-1}
Ethanol concentration	1.0 M
Oxygen flow	20 ml min^{-1}
Oxygen purity	98%
Oxygen backpressure	15 + 2 psi
Relative humidity	>90%

trode assembly (MEA) [21]. After hot pressing, the decal was removed to form the MEA. The MEA was maintained at 80 °C for 2 h in 0.5 M sulfuric acid followed by immersion in 80 °C deionized water by 2 more hours. After, the MEA was dried on a heated table at 60 °C for 30 min.

Each fabricated MEA was settled in a housing block with gas diffusion area of 5 cm^2 and evaluated in a fuel cell test station (Electrochem Inc.®). The experimental conditions for the fuel cell test are reported in Table 1.

3. Results and discussion

Table 2 provides a summary of EDX analysis for the prepared electrocatalysts. The measured atomic ratios of bi-metallic mixtures were close to nominal atomic ratios, which is indicative of the accuracy of the ethylene–glycol-method in reducing all metals present in the precursor solutions. In the case of tri-metallic mixtures, the atomic ratios are less concordant with the nominal ratios. Despite this fact, all EDX analysis report an acceptable agreement between the nominal and obtained atomic ratios, which is why the ethylene–glycol-method is considered a versatile and efficient technique for reducing different types of metal over the used support. Particularly in the tri-metallic mixtures, supports that contain nickel (like Pt$_{75}$Ru$_{15}$Ni$_{10}$/C) show a very good agreement between nominal and measured atomic ratios.

The catalytic activity for ethanol oxidation was determined by comparing the current reached in the positive sweep at 700 mV versus NHE from CV curves (Figs. 1 and 2).

Figs. 1 and 2 show that the addition of nickel to Pt–Ru mixtures significantly increases the catalytic activity. The current

Table 2
Nominal and EDX atomic ratios for electrocatalysts

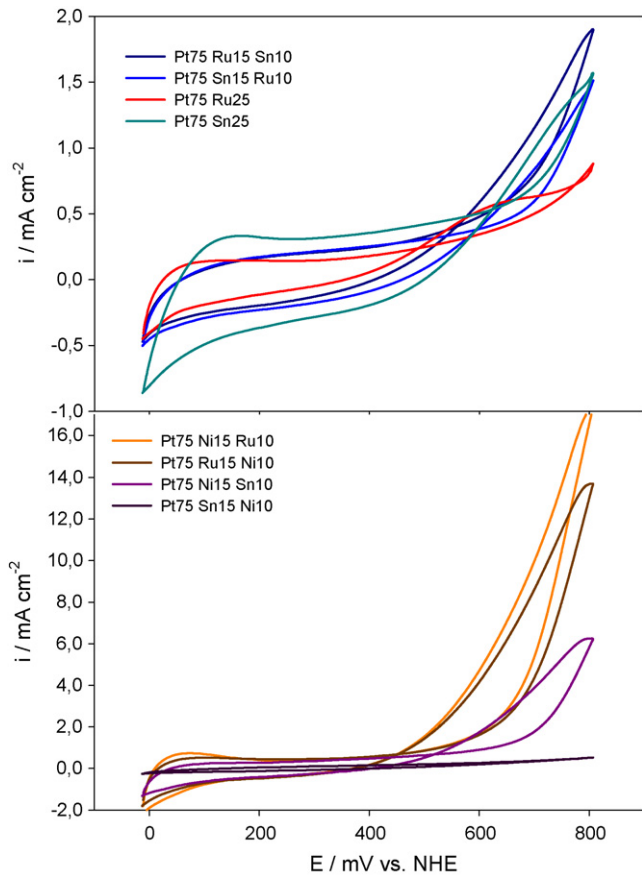| Electrocatalyst	Nominal atomic ratio			EDX atomic ratio		
	Pt	2° metal	3° metal	Pt	2° metal	3° metal
PtRu/C	85	15	–	84.6	15.4	–
PtSn/C	85	15	–	85.0	15.0	–
PtRu/C	75	25	–	76.1	23.9	–
PtSn/C	75	25	–	75.2	24.8	–
PtRuSn/C	75	15	10	80.6	7.1	12.2
PtSnRu/C	75	15	10	70.8	17.7	11.5
PtRuNi/C	75	15	10	74.3	15.2	10.5
PtNiRu/C	75	15	10	78.6	11.1	10.3
PtSnNi/C	75	15	10	78.2	11.2	10.6
PtNiSn/C	75	15	10	73.5	15.3	11.2

Fig. 1. Cyclic voltammetries for ethanol (1.0 M) at 50 °C.

reached using Pt–Ru–Ni catalysts is around five times greater than that obtained in other mixtures. The $Pt_{75}Ni_{15}Sn_{10}$ electrocatalyst also increases the catalytic activity by a factor of two, as compared to the Pt–Sn mixtures. The Pt–Ru–Sn mixtures show a catalytic activity similar to the bi-metallic mixtures and slightly higher than $Pt_{75}Sn_{15}Ni_{10}/C$ catalysts. The bi-metallic mixtures show a lower catalytic activity than mixtures containing nickel.

The results obtained using direct ethanol fuel cells in terms of potential–current density curves and power density–current density curves are shown in Figs. 3 and 4, respectively. When
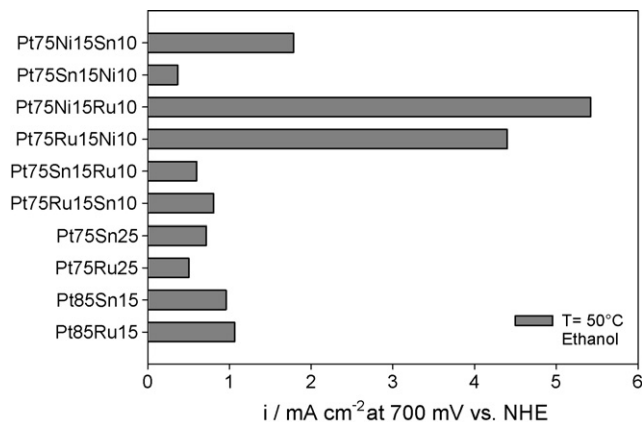
Fig. 2. Catalytic activity for ethanol (1.0 M) electrooxidation at 50 °C.
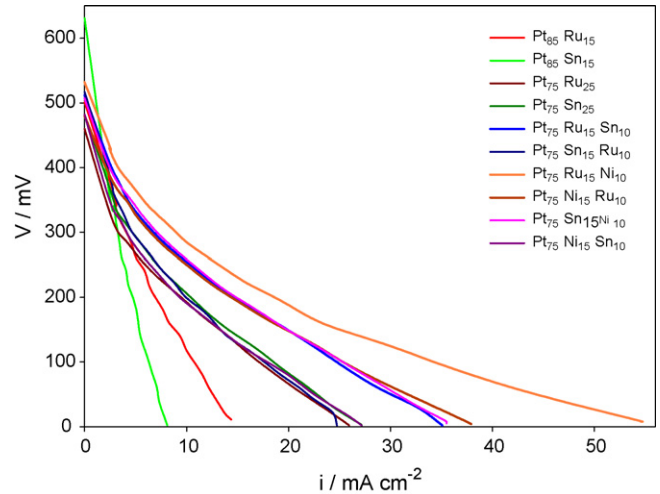

Fig. 3. Potential–current density curves of single fuel cells with different anode electrocatalysts at Table 1 conditions.

Pt–Ru–Ni catalysts were used in the anode, remarkable enhancement in cell performance was observed. Pt–Ru–Ni performed better than all other catalysts. These results are in agreement with CV results that demonstrate a higher activity of Pt–Ru–Ni at higher potentials. On the other hand, with Ni addition to Pt–Sn mixtures, the current density increased.

According to power density–current density curves, the best performance corresponds to DEFC with $Pt_{75}Ru_{15}Ni_{10}/C$ electrocatalysts in their anode. Also, the DEFCs with tri-metallic mixtures in the anode (i.e., $Pt_{75}Ni_{15}Ru_{10}/C$, $Pt_{75}Sn_{15}Ni_{10}/C$ and $Pt_{75}Ru_{15}Sn_{10}/C$) demonstrate a higher performance, as compared to fuel cells with other electrocatalysts in the anode (e.g., bi-metallic anodes with atomic ratio of 85:15).

To compare all assembled MEAs, the current used to reach a voltage of 200 mV was evaluated in each fuel cell (Fig. 5). At this voltage, it is assumed that there are neither mass nor electronic transfer problems. Additionally, the highest current reached in the fuel cell evaluation is depicted in Fig. 6.
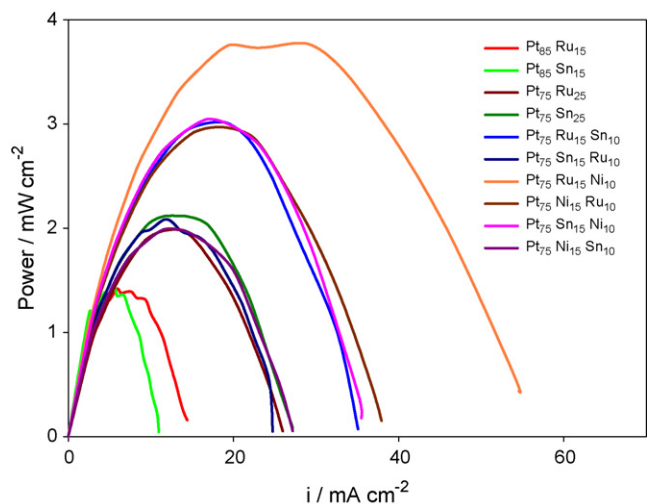

Fig. 4. Power density–current density curves of single fuel cells with different anode electrocatalysts at Table 1 conditions.
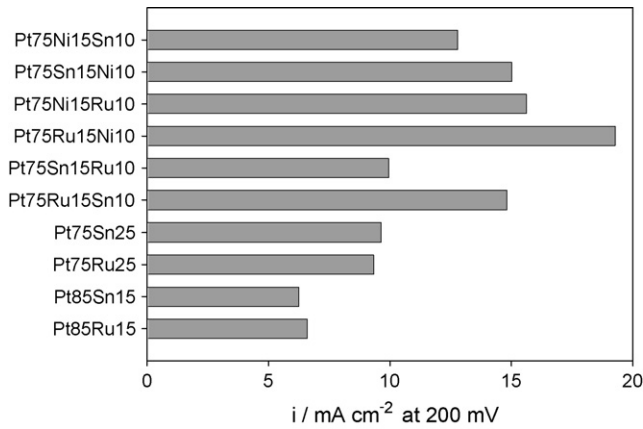
Fig. 5. Performance of DEFCs with different anode catalysts at 200 mV and Table 1 conditions.

For bi-metallic catalysts, results demonstrate that the current obtained in Pt–Ru and Pt–Sn mixtures is similar. However, when the amount of platinum is decreased and ruthenium or tin are increased, a moderate increase in the current is obtained. On the other hand, the tri-metallic catalytic mixtures produced higher currents relative to bi-metallic catalysts.

Among tri-metallic catalytic mixtures, a higher performance was obtained using the nickel containing electrocatalysts. In particular, the Pt–Ru–Ni mixtures demonstrate a higher current output when used as anodes in DEFCs. Similarly, the Pt–Sn–Ni electrocatalysts show an interesting performance and the Pt–Ru–Sn mixtures show currents that are minimally higher than those obtained in bi-metallic mixtures. This demonstrates that the addition of nickel to the electrocatalysts improves DEFC performance with respect to other catalytic mixtures, which were investigated as anodes for these devices.

With respect to variations in the atomic ratio of Pt–Ru–Sn catalytic mixtures (e.g., 75:15:10 or 75:10:15), we observed that the better performing catalytic mixture has a higher Ru content, and the same is observed for the Pt–Ru–Ni electrocatalyst.

Performance ranking of the ten investigated electrocatalysts in DEFCs under the same experimental and evaluation conditions is depicted in Fig. 7.
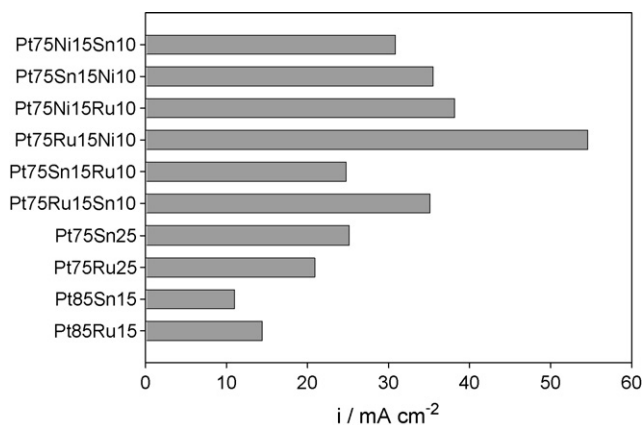

Fig. 6. Performance of DEFCs with different anode catalysts at highest current density and Table 1 conditions.
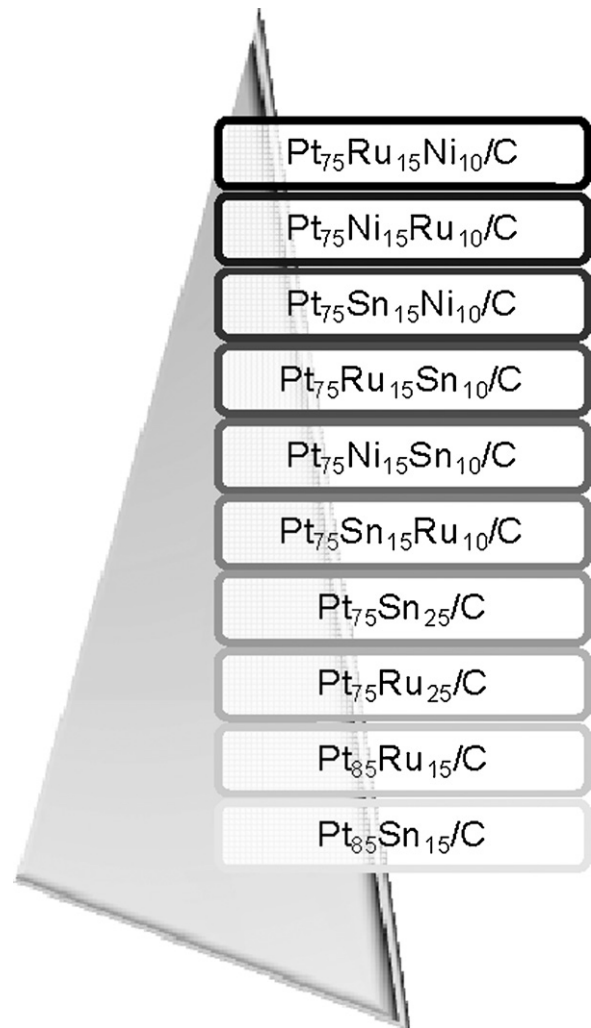

Fig. 7. Electrocatalysts performance ranking in the DEFCs.

4. Conclusions

The evaluation of 10 different catalytic mixtures for ethanol oxidation demonstrates that nickel addition to the anode improves DEFC performance for the investigated catalytic mixtures. When $Pt_{75}Ru_{15}Ni_{10}/C$ is used as an anode catalyst, the current density obtained in the fuel cell is higher than that obtained in all other investigated catalysts. In the same manner, we demonstrated that tri-metallic catalytic mixtures perform better than bi-metallic catalysts. These results are in agreement with CV results that show a higher activity of Pt–Ru–Ni at higher potentials.

Acknowledgements

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