91 compositions simultaneously screened for ethanol oxidation.

Single cell performance of the best compositions.

**Combinatorial PtSnM (M = Fe, Ni, Ru and Pd) nanoparticle catalyst library
toward ethanol electrooxidation**

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Abstract

Electrode arrays containing 91 combinations of Pt-Sn-M (M = Fe, Ni, Pd, and Ru) were prepared by borohydride reduction of aqueous metal salts on carbon paper, and screened by fluorescence assay for activity as ethanol electrooxidation catalysts. Catalysts that showed high activity for this reaction were identified as being Pt(80)Sn(10)Fe(10), Pt(80)Sn(10)Ni(10), Pt(70)Sn(20)Pd(10), and Pt(70)Sn(10)Ru(20) (numbers in parenthesis indicate atomic percent). These were significantly more active than Pt or PtSn catalysts, also present in the electrode arrays. These 4 compositions were synthesized as nanoparticles and characterized physically and electrochemically. X-ray diffraction showed a Pt face-centered cubic (fcc) structure with an average crystallite size of about 2.0 nm for all catalysts. The electrochemical tests for the oxidation of ethanol revealed excellent electrocatalytic activity and single cell (fuel cell) power density for all four catalyst formulations. Fe-containing catalysts exhibited the highest activity ($13 \text{ A g}_{\text{Pt}}^{-1}$) and single-cell performance (50 mW cm^{-2}) followed by Ni- and Pd-containing materials with similar results; electrocatalytic activity around $10 \text{ A g}_{\text{Pt}}^{-1}$ and power densities of 43 mW cm^{-2} . The lowest performance was observed for the Ru-containing catalyst. However, its single-cell performance (30 mW cm^{-2}) was still comparable to that of the commercial PtSn-Etek electrocatalyst.

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1. Introduction

The development of an efficient material for the electrooxidation of ethanol continues to be a major challenge in fuel cell research [1-7]. In acidic media, Pt-based catalysts are still considered to be the best materials for this purpose. However, it is well known that pure Pt does not exhibit good catalytic activity due to poisoning by intermediates (including CO) generated during ethanol electrooxidation. This, in turn, requires the application of higher overpotentials for the oxidation of ethanol [2, 8, 9]. Thus, one of the main goals of fuel cell electrocatalysis is the development of active electrocatalysts that can perform ethanol oxidation at lower potentials [10-12]. Currently, there has been a great deal of effort placed on the development of better-performing catalysts by combining Pt with other metals, typically first row transition metals to enhance electrocatalytic activity [13-17].

Due to the growing demand for functional materials that can be employed in modern science and technology, one way to reduce time and cost when searching for better-performing materials is to apply high-throughput methods. Combinatorial methods enable efficient, rapid, and low cost screening when compared to traditional methods.

In the field of electrocatalysis, Reddington et al. [18] were the first to demonstrate an effective method for screening several compositions simultaneously, based on a combination of electrochemical and fluorescence measurements. Since then, combinatorial methods have received growing attention [19, 20]. Combinatorial screening allows for the rapid screening of electrocatalysts, including materials that can be used as anode or cathode catalysts in low-temperature polymer electrolyte membrane fuel cells (PEM-FC). The simultaneous synthesis and screening of a large number of

potentially active catalysts is a very attractive approach to develop an ideal composition that can be employed in PEM-DEFCs (direct ethanol fuel cells).

The coupling of electrochemical measurements and screening techniques has played an important role in developing new catalysts for application in fuel cells [21-27]. Fluorescence assays have been especially useful in activity-mapping of these materials due to their facile experimentation in aqueous medium and in the presence of the target fuel. Fluorescence screening assays are often based on pH-sensitive dyes whose fluorescence intensity changes within a certain pH range [28]. When ethanol is oxidized at an electrode surface, protons are generated, resulting in a drop in the local pH [7, 17, 29]. The generated protons (H^+) can react with a proton-sensitive fluorescent dye (e.g. quinine), causing it to fluoresce. As a consequence, regions on the surface of the catalyst library with higher catalytic activity will exhibit intense fluorescence at lower applied potentials. After identification via screening, the materials comprising the bright (and most active) spots can be characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM), thus providing valuable information about composition, structure, and morphology.

The literature contains many examples of the combinatorial investigation of methanol electrooxidation [18, 26, 30, 31]. However, a much more limited number of investigations have been focused on ethanol oxidation. Recently, Chu and Shul [32] applied combinatorial chemistry to the screening of 66 PtRuSn-anode arrays for the oxidation of methanol, ethanol, and 2-propanol. The screening was performed employing quinine as a fluorescence indicator of catalytic activity, which allowed for the selection of the optimal electrocatalyst composition. PtRuSn (80:20:0), PtRuSn (50:0:50), and PtRuSn (50:30:20) yielded the lowest onset potentials for methanol, ethanol, and 2-propanol electro-oxidation, respectively, according to their CV results.

Tague et al. [33] studied combinatorial libraries of Pt-M alloy (M = a wide variety (18 different) of metals) thin films for methanol and ethanol electrooxidation. Films were prepared using a combinatorial sputter deposition system and screened by a fluorescence assay. They found that platinum films, with less than 5 % of Fe, Sn, In, Ni, Zn and Ru, had the most significant influence on the catalytic activity for both alcohols investigated.

Our research activities aim to enhance the existing combinatorial knowledge base for ethanol oxidation, given the small number of publications in the literature. We have prepared binary and ternary materials of the general type Pt-Sn-M (M = Fe, Ni, Ru and Pd) and surveyed their activity towards the electrooxidation of ethanol. Additionally, we have carried out extensive physical and electrochemical characterization to assess the performance of the most active catalysts. We have also carried out single-cell fuel cell studies

2. Experimental

2.1 Combinatorial

The nanoparticle combinatorial library was constructed as described in [31]. Briefly, PtSnM (M = Fe, Ni, Ru and Pd) electrode arrays were prepared by dispersing 0.25 M water/ethanol solutions of the metal salts (H_2PtCl_6 , RuCl_3 , PdCl_2 , Aldrich, SnCl_2 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Mallinckrodt) onto a Teflon-coated Toray[®] carbon sheet, using manually prepared solution mixtures at the desired metal molar ratios. The molar percentages of Pt for each PtSnM group were 90, 80, 70, and 60%. The completed array was reduced with a 5 wt. % sodium borohydride solution, and the reduced array was thoroughly washed with nanopure water and dried at 50° C in a

vacuum oven for 12 hours. Fig 1 shows the catalyst array disposition on the carbon support and the investigated composition map.

Figure 1

The fluorescence assay described in [33] was employed to assess the catalytic properties of the Pt-based catalysts. A Teflon electrochemical cell was sealed with an o-ring atop a 3-inch diameter catalyst array. Copper contacts were mechanically pressed against the carbon paper beyond the outer diameter of the o-ring to avoid contact with the testing solutions. A coiled gold counter electrode was placed approximately 1 cm above the sample and the entire cell was sealed with a quartz plate on the top with a hole to hold a Ag/AgCl reference electrode.

The standard testing procedure required filling the electrochemical cell with a neutral pH aqueous solution of 0.3 mM quinine, 0.1 M potassium triflate, and 6.0 M ethanol. The potential was scanned, at 5 mV s^{-1} , from the open circuit potential to ca. 900 mV vs. NHE. Upon oxidation of the fuel, the generated protons decreased the local pH at the working electrode (the electrode array) below pH 5, enabling quinine fluorescence to be observed under UV illumination. Images were collected at 20 mV intervals with a CCD camera, and a fluorescence onset potential, defined as the potential at which the fluorescence was first observed, was established. To ensure that the observed response was not from any oxidation processes occurring at the surface of the composition film, a background solution (without fuel) was added to the cell and the potential was scanned over the same potential range. The most active compositions were selected based on their onset potentials.

2.2 Electrocatalysts preparation

Four carbon supported Pt-based catalysts, selected after fluorescence screening, including Pt(80)Sn(10)Fe(10)/C, Pt(80)Sn(10)Ni(10), Pt(70)Sn(20)Pd(10) and Pt(70)Sn(10)Ru(20) were prepared for further electrochemical characterization. Catalysts with 40 wt. % metal loading were prepared by NaBH₄ reduction. Pre-determined amounts of metal precursors (H₂PtCl₆, RuCl₃, PdCl₂, Aldrich, SnCl₂, NiCl₂•6H₂O, FeCl₃•6H₂O, Mallinckrodt) in aqueous solution (0.05 M) were mixed in 25 mL of ethylene glycol and the pH was adjusted to 10 with 3.0 M NaOH. The mixture was stirred for 10 minutes in an ultrasonic bath. Subsequently, enough Vulcan XC-72 carbon powder was added to the mixture in order to achieve catalysts with the desired metal loading. Afterwards, 5 mL of 0.15 M NaBH₄ were added dropwise and the mixture was stirred for 12 hours to support the reduced nanoparticles. Finally, the suspension was filtered and washed with water and the solid product was dried at 120°C for 2 hours in an oven under a N₂ atmosphere.

2.3. Physical Characterization

X-ray diffraction patterns of the catalysts were obtained with a Rigaku diffractometer operating with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) generated at 40 kV and 40 mA. Scans were done at 5° min^{-1} for 2θ values between 20 and 90° . The crystallite size and the apparent lattice parameter were estimated by using the Scherrer equation (1) and equation (2), using the (220) plane as a reference:

$$D = \sqrt{2} \lambda / B \cos \theta_B \quad (1)$$

$$a = \sqrt{2} \lambda / \sin \theta \quad (2)$$

Bulk particle and surface compositions were analyzed via energy dispersive X-ray spectroscopy (EDX) using a Leica microscope Zeiss LEO 440 model SEM coupled to an Oxford 7060 model analyzer and X-ray Photoelectron Spectroscopy (XPS) using Surface Science Instrument SSX-100, respectively.

2.3. Electrochemical measurements

The background electrochemical profile of the catalysts was obtained by cyclic voltammetry (CV) in N₂ purged 0.05 M H₂SO₄. Measurements were conducted with a PAR 273 potentiostat in a conventional electrochemical cell using a reversible hydrogen electrode (RHE) and a platinum wire as reference and counter electrodes, respectively. To perform the electrochemical measurements, specified amounts of the catalyst powder were dispersed into a solution (100 μ L) consisting of isopropanol (95 μ L) and Nafion[®] (5 μ L) (5 % wt. in aliphatic alcohols). The mixture was homogenized in an ultrasonic bath for 10 minutes. After homogenization, 10 μ L of the catalystst ink were deposited onto a previously polished glassy carbon disk electrode (0.196 cm²). In all the cases, the catalyst layer had a metal loading of 0.1 mg_{Pt} cm⁻². Activity and stability tests were carried out by cyclic voltammetry and chronoamperometry in the presence of 1.0 M ethanol and 0.05 M H₂SO₄.

Fuel cell testing was carried out using membrane electrode assemblies (MEAs) prepared by hot-pressing a pretreated Nafion[®] 117 membrane placed between an E-TEK cathode (2 mg_{Pt} cm⁻²) and a homemade anode (2 mg_{Pt} cm⁻²) at 130 °C for 90 s, under a pressure of 35 kg cm⁻². The operating fuel cell performances were determined in a single DEFC with a geometric electrode surface area of 5.3 cm² using a test bench (Eletrocell). The temperature of the fuel cell and the oxygen humidifier were set at 85°C and 80, respectively. The ethanol and oxygen pressures were fixed at 1 and 3 bar,

respectively. The ethanol concentration was kept constant at 2.0 M. Curves of the cell voltage (V) versus current density j (mA cm^{-2}) as well as power density (mW cm^{-2}) versus current density j (mA cm^{-2}) were recorded.

3. Results and Discussion

Fig. 2 presents the fluorescence results for PtSnM (M = Fe, Ni, Ru and Pd) electrode arrays for ethanol electrooxidation at different potentials: (A) +0.27 V, (B) +0.46 V, and (C) +0.93V against a RHE reference electrode. At low potentials, only a few spots fluoresced, revealing the most active ones (Fig. 2A). As the potential was scanned to higher values, more spots fluoresced and when the highest potential was achieved, virtually all spots were active for ethanol electrooxidation (Fig. 2C). Fig. 2D presents the fluorescence intensity map vs. potential of the evaluated compositions where a significant fluorescence intensity, relative to the background, can be correlated to the onset potential (E_{onset}) of the reaction (scale on the right) allowing a more precise determination of the most active compositions for ethanol oxidation. While the fluorescence assay was used for screening for electrocatalytic activity, the results can be considered semi-quantitative since there are clear differences in the fluorescence intensity as a function of potential, as is evident in panels A-C in figure 2. In addition, the onset potential for the different compositions, presented in Fig. 2D, provides a means of identifying and selecting the most active compositions.

In general, the binary Pt-M compositions were not very active towards ethanol electrooxidation. They presented E_{onset} values that were about 300 mV more positive than the onset values of ternaries containing Sn. From the map, the most active catalysts, Pt(80)Sn(10)Fe(10), Pt(80)Sn(10)Ni(10), Pt(70)Sn(20)Pd(10) and Pt(70)Sn(10)Ru(20), were selected for further study.

Figure 2

The bulk composition of the different carbon-supported PtSn-based catalysts was determined by EDX analysis and the results are presented in Table 1. Even considering that EDX generally only provides semi-quantitative information, we obtained a reasonable agreement between experimental compositions and the nominal ones for almost all of the catalysts, except for the Pt(80)Sn(10)Ni(10) which only showed a 2% Ni content, compared to the expected value of 10 %. Hereafter, we will use the experimental bulk composition determined by EDX to represent the catalysts.

Table 1

The diffraction patterns and the structural profiles of the catalysts obtained by XRD are shown in Fig. 3. The broad peak at $2\theta = 25^\circ$ was attributed to the (002) plane of the carbon support. The other observed peaks around 39° , 46° , 68° , 81° and 86° are characteristic of the crystalline structure of face-centered cubic (fcc) Pt (space group Fm-3m) and refer to the (111), (200), (220), (311), and (222) planes, respectively. The average crystallite size was about 2.0 nm for all catalysts and the lattice parameter did not differ significantly from that of pure Pt (3.923 Å).

Addition of Sn, together with a third metal, did not shift the 2θ values of the diffraction peaks substantially, likely because the radii of these atoms affect the Pt structure in opposite ways. Sn (1.45 Å) atoms are larger than Pt (1.39 Å) atoms and cause the lattice to expand, shifting the reflection planes toward lower 2θ values. Atoms smaller than Pt, such as Ni (1.24 Å), Ru (1.34 Å), Fe (1.26 Å) and Pd (1.37 Å), make the lattice contract, shifting the reflection planes toward higher 2θ values. Although

EDX analysis indicated that the three metal elements were present in each composition, it is difficult to draw conclusions about the nature of their structure because of the counter-balancing effects of the non-Pt metals as described above.

Figure 3

XPS was performed to analyze the electronic structure of the various components in the different catalysts synthesized. All catalysts were submitted to a survey scan to determine the surface composition. The analysis showed that, in addition to Pt, the main elements for all of them were ruthenium, palladium, tin, carbon and oxygen. The presence of Ni and Fe was not evident in the spectra, and the Pd 3d peak overlapped with the Pt 4f region, complicating quantitative analysis. Only in the case of PtSnRu was it possible to quantify the composition of the surface of the catalyst, which exhibited good agreement with EDX analysis. The electronic structure of the catalyst particles was determined by recording XPS scans over narrow energetic regions corresponding to the core levels of Pt 4f (Fig. 4A) and Sn 3d (Fig. 4B). For this analysis, all of the spectra were corrected to the C 1s peak at a BE of 284.8 eV.

Fig. 4A shows a representative spectrum of the Pt 4f core levels obtained from the PtSnPd composition deconvolved into three sets of spin-orbit doublets fitted by constraining the spin-orbit separation of 3.2 eV, which corresponds to Pt 4f_{7/2} and 4f_{5/2} of different oxidation states. The most intense doublet, with BEs of 70.7 and 73.9 eV, corresponds to Pt (4f_{7/2,5/2}) peaks and is due to metallic Pt, shifted to lower BE values compared to the literature values of 71.2 and 74.5 eV [34]. This displacement in the BE suggests that the surface layers of the catalyst are likely an alloy rather than discrete particles of the pure elements, as a change in BE, from the pure element, is often the result of partial electron transfer between the elements in an alloy, likely due to work

function differences [35]. This is also consistent with XRD analysis which also suggests alloy formation among the metal constituents of the catalysts. The BE peaks at 71.5 and 74.8 eV and the peaks at 72.5 and 76.4 eV, seen in the deconvolved spectrum, correspond to Pt ($4f_{7/2,5/2}$) peaks of Pt (II) as in PtO or Pt(OH)₂ and Pt (IV) as in PtO₂ species, respectively [36-38]. All Pt-species were observed for all compositions investigated with a similar BE and the relative intensities of the Pt (0), Pt(II) and Pt(IV) chemical states were around 57%, 30% and 13% for all of them, respectively. The chemical state of tin in the catalysts was refined with spectra of Sn 3p core levels as shown in Fig. 4B. The XPS spectra were deconvolved into two components Sn 3p_{3/2} and Sn 3p_{5/2}. The peaks at 485.7 and 493.7 eV correspond to Sn ($3d_{3/2,5/2}$) of tin in the zero-valence state, whereas the second pair of peaks at 487.0 and 495.4 can be assigned to the oxidized species of Sn(II/IV) [38]. The binding energies of Sn are slightly higher than reference data, likely due to interactions between Sn and Pt. The presence of SnO₂ in the vicinity of Pt nanoparticles is thought to play an important role for ethanol and CO oxidation, enhancing catalytic activity. The same analysis was made for all PtSnM catalysts and the results showed about 50% of SnO₂ for all of them.

Figure 4 A-B

3.2 Electrochemical Characterization

Cyclic voltammetric (CV) profiles of all PtSnM catalysts in 0.05 M H₂SO₄ solution are presented in Fig. 5. All catalysts investigated exhibited a very similar voltammetric profile. In general, we observed very poorly-defined H₂ adsorption/desorption peaks in the potential region between +0.05 to +0.40 V vs RHE in comparison to the well-defined hydrogen peaks for polycrystalline Pt as well as the commercial Pt/C catalyst. This behavior can be attributed, at least in part, to the presence of Sn that covers part of

the Pt-sites suppressing the H₂ adsorption/desorption peaks as discussed by Furuya et al [39]. Furthermore, the cyclic voltammograms for the PtSnM/C catalysts showed an increase in current density in the double layer region (+0.4 to +0.85 V), which could be related to the presence of transition metals that are responsible for the activation of H₂O. Indeed, XPS analysis indicated the presence of Sn, SnO_x, and Ru species, all of which have a strong contribution on the catalysis mechanism of small organic molecules by activating H₂O on their surfaces at reduced overpotentials compared to pure Pt, which leads to high capacitive charging currents in the double layer region [40-43]. Fig. 5 also shows a reversible peak around +0.75 V for all catalysts in the forward (positive-going) scans and in the reverse scan at around +0.6 V that corresponds to O₂ adsorption (equations (3) to (6)) and desorption (equations (7) and (8)) on Sn and Sn oxide surfaces from the dissociation of H₂O [38, 42, 44].

The role proposed above can be also be played by Ru, Pd, and Pt since they are able to activate water on their surfaces. On the other hand, Fe and Ni are not able to activate water on their surfaces in acidic media.

The region corresponding to formation/reduction of PtO is very poorly-defined because the potential limit on the CV was set at +1.0 V, i.e., before considerable amount

of PtO has been formed, considering that this species is formed at potentials ranging between +0.8 to +1.4 V and presents its reduction peak around +0.8 V on the reverse (negative-going) scan.

Figure 5

Fig. 6 shows the voltammetric curves for the electrocatalysts in the presence of 1.0 M ethanol. Hydrogen adsorption/desorption peaks are clearly suppressed by the ethanol adsorption in the lower potential range (+0.05 to +0.2 V vs RHE). At around +0.2 V ethanol starts to be oxidized as a consequence of ethanol molecules being adsorbed on Pt sites, forming acetaldehyde as represented by equations (9) and (10) [7, 45].

The formation of higher oxidation state products such as acetic acid (4 electrons, equations (11) to (13)) and CO₂ (2 electrons, equations (14) and (15)) occurs at high ($E > 0.8$ V vs RHE) and low potentials ($E < 0.4$ V), respectively. However, both mechanisms involve water activation on the Pt surface that occurs at intermediate potentials ($0.6 \text{ V} < E < 0.8 \text{ V}$) because oxygenated species are required to form these products [46].

On step (12), the presence of Sn and the third metal on PtSnM catalysts presented a significant contribution to the efficiency of ethanol oxidation. PtSn-based compositions containing Fe, Ni, and Pd started to oxidize ethanol molecules around +0.19 V vs RHE while the composition containing Ru presented an onset potential for ethanol oxidation (E_{onset}) around +0.24 V vs RHE, evidence that Ru's contribution to the ethanol catalysis is less effective than the other co-metals added to PtSn. However, all of them exhibited E_{onset} values significantly less positive than pure Pt (+0.45 V vs RHE) [17, 47].

The increase in current density by the catalysts containing Fe, Ni and Pd at low potentials for ethanol electrooxidation can be explained firstly by the presence of Sn, which promotes ethanol oxidation by either an electronic effect in the Pt-based electrode material or by activation of interfacial water molecules at lower potentials compared to a pure Pt catalyst. As explained before, oxygenated species from water are necessary to complete the oxidation of adsorbed reaction intermediates leading to the formation of acetic acid and CO_2 . Secondly, the presence of a third metal on the PtSn-based compositions can also affect electrocatalytic activity. Fe and Ni can exert an electronic effect on Pt and Sn atoms caused by their low electronegativity (1.83 and 1.91, respectively) that can boost the oxophilic character of the surface, modify the -OH adsorption energy and the concentration of this species on the catalyst surface which enhance the water activation on Pt and Sn, resulting in ethanol oxidation at lower potentials [22, 48]. Pd presents a similar catalytic behavior to Pt. However, its high

tolerance to CO poisoning contributes to rapidly converting CO to CO₂ and improving the ethanol oxidation turnover [49-51]. Ru acts by the same mechanism as Sn. However, in this study Ru did not present a significant contribution to ethanol oxidation when compared to the other co-catalysts.

Figure 6

Chronoamperometry can be a more effective way to evaluate the electrocatalytic performance of the electrodes for ethanol oxidation at low potentials and under long-term operation conditions. Thus, 30-minute chronoamperometry at a fixed potential of +0.40 V vs RHE was recorded in the presence of 1.0 M ethanol. Fig. 7 shows the current-time curves for the catalysts investigated, with currents normalized to the Pt content. Initially we observed a rapid drop in current due to the poisoning of the Pt-sites by ethanol by-products. After that, the current decreased slowly and the reaction turnover became dependent on the adsorption of new ethanol molecules on the remaining Pt-sites.

Chroamperometry also presented a good agreement with the cyclic voltammetry experiments. PtSnFe presented the highest catalytic activity for ethanol electrooxidation (13.2 A g_{Pt}⁻¹) followed by PtSnNi (10.6 A g_{Pt}⁻¹), PtSnPd (9.3 A g_{Pt}⁻¹), and PtSnRu (3.1 A g_{Pt}⁻¹). This confirms our initial findings which showed that PtSnM catalysts are strongly related to the Sn and third metal effects on the Pt catalyst.

Figure 7

The electrochemical surface area (ECSA) of the PtSnM catalysts was investigated by CO stripping voltammetry in 0.05 M H₂SO₄ at 10 mV s⁻¹, and the

results are shown in Table 2. The E_{onset} for CO oxidation occurs at around +0.35 V vs RHE and the ECSAs are very similar for all catalysts investigated, ranging from 31.0 to 41.0 $\text{m}^2 \text{g}_{\text{Pt}}^{-1}$. PtSnFe and PtSnNi exhibited the highest ECSA, both 41.0 $\text{m}^2 \text{g}_{\text{Pt}}^{-1}$. However, PtSnPd and PtSnRu also displayed considerable ECSA of 36 and 31 $\text{m}^2 \text{g}_{\text{Pt}}^{-1}$, respectively.

Table 2

Finally, we carried out single-cell (fuel cell) tests with the best-performing PtSnM catalyst. Fig. 8A shows J–V curves for the PtSnM/C and commercial PtSn-Etek catalysts. The open-circuit voltage (OCV) of the single-cells using PtSnM/C catalysts and the commercial PtSn-Etek had significant differences. All compositions exhibited OCVs higher than that of commercial PtSn-Etek (0.58 V). The highest OCV values were observed for PtSnPd (0.76 V), PtSnFe (0.73 V) and PtSnNi (0.72 V). These catalysts also presented lower polarization losses in the single-cell tests when compared to the commercial PtSn catalyst (Etek) as well as PtSnRu. These observations correlate to higher power densities as can be seen in Fig. 8B.

PtSnFe showed the best single-cell performance, exhibiting a power density of 50 mW cm^{-2} . PtSnNi and PtSnPd also exhibited significant power densities of 43 mW cm^{-2} . These results are very promising considering that these tests were done at a lower temperature (80 °C) compared with other results reported in the literature (shown in Table 3) where most of the single-cell test were carried out at 90 °C. In summary, virtually all of our PtSnM catalysts presented superior power densities when compared to PtSn-Etek. The only exception was PtSnRu, which exhibited the same power density of the commercial composition (30 mW cm^{-2}). Moreover, the power densities achieved

in this investigation are comparable and even superior to many presented in the literature, justifying these compositions as promising anode catalysts for DEFC.

Figure 8 A-B

Table 3

4. Conclusions

In the present study, combinatorial methods were applied to screen 91 different compositions of Pt-Sn-M (M = Fe, Ni, Pd and Ru) as electrocatalysts for ethanol electrooxidation. The fluorescence screening indicated that ternary compositions PtSnM were more active than PtSn and binary PtM. Four compositions, Pt(80)Sn(10)Fe(10), Pt(80)Sn(10)Ni(10), Pt(70)Sn(20)Pd(10) and Pt(70)Sn(10)Ru(20), were chosen for their electrocatalytic activity to ethanol electrooxidation and synthesized for more detailed electrochemical tests. EDX and XRD characterizations indicated that the active catalyst compositions were close to the intended (nominal) values, except for PtSnNi which exhibited low Ni levels; 2 at. % vs 10 at. %. All the catalysts had an FCC structure (Pt) with crystallite sizes around 2.0 nm. Nanoparticle surface analysis by XPS revealed Pt and Sn in different oxidation states corresponding to metallic and oxidized forms of these metals. The presence of the third metal was generally not observed on the surface of the catalysts. Electrochemical tests matched the combinatorial electrochemistry results. The four catalysts investigated presented excellent catalytic activity and power density towards ethanol electrooxidation showing that these compositions are promising as anodes in DEFC. Combinatorial chemistry is an efficient and important tool to discover new active materials for DEFC.

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Figure Captions

Figure 1. Combinatorial catalyst array for ethanol electrooxidation and composition map of the synthesized PtSnM (M = Fe, Ni, Pd, and Ru). Red spots indicate the compositions investigated.

Figure 2. Combinatorial array and screening results by fluorescence imaging of PtSnM (M = Fe, Ni, Ru and Pd) electrode arrays in 6.0 M ethanol and quinine fluorescent indicator. Active compositions for ethanol electrooxidation are shown as bright spots: fluorescence image at (A) lower overpotential ($\sim 0.27\text{V}$ vs. RHE); (B) intermediate overpotential ($\sim 0.46\text{V}$ vs. RHE) and (C) high overpotential ($\sim 0.93\text{V}$ vs RHE); (D) Fluorescence onset potential for ethanol electrooxidation of PtM and PtSnM library.

Figure 3. XRD patterns of the carbon supported PtSn-based materials prepared by NaBH_4 reduction.

Figure 4. Representative spectra of core levels of Pt 4f (A) and Sn 3d (B) for PtSnM catalysts.

Figure 5. Cyclic voltammograms of the PtSnM catalysts recorded in 0.05 M H_2SO_4 at 10 mV s^{-1} .

Figure 6. Cyclic voltammograms of the PtSnM catalysts recorded in 0.05 M H_2SO_4 + 1.0 M EtOH at 10 mV s^{-1} .

Figure 7. Current-time (chronoamperometric) curves of the PtSnM catalysts recorded in 0.05 M H_2SO_4 + 1.0 M EtOH at 0.4 V vs RHE for 30 minutes.

Figure 8. (A) Cell voltage and (B) power density vs current density for DEFC. Electrode area: 5.29 cm^2 area, at $80\text{ }^\circ\text{C}$ using the PtSnM/C and PtSn-Etek anodes and Pt/C cathode ($2\text{ mg}_{\text{Pt}}\text{ cm}^{-2}$ catalyst loading, 60 wt.% catalyst on carbon). $P(\text{O}_2) = 3\text{ bar}$; $P(\text{EtOH}) = 1\text{ bar}$; $[\text{EtOH}] = 2.0\text{ M}$; Nafion[®] 117 membrane.

Table 1. EDX and XRD results of PtSnM catalysts

Catalyst	Lattice constant (Å)	Crystallite Size (nm)	Pt:Sn:M (EDX)
Pt(80)Sn(10)Fe(10)	3.922	2.0	79:15:06
Pt(80)Sn(10)Ni(10)	3.918	2.3	79:19:02
Pt(70)Sn(10)Ru(20)	3.917	2.1	71:14:15
Pt(70)Sn(20)Pd(10)	3.908	2.4	69:21:10

Table 2. Electrochemical parameters of PtSnM catalysts

Catalysts	E_{onset} / V	Catalytic activity/ $A\ g_{Pt}^{-1}$	ECSA / $m^2\ g_{Pt}^{-1}$
Pt(79)Sn(15)Fe(06)	0.18	13.2	41.0
Pt(79)Sn(19)Ni(02)	0.19	10.6	41.0
Pt(69)Sn(21)Pd(10)	0.19	9.3	36.0
Pt(71)Sn(14)Ru(15)	0.24	3.1	31.0

Table 3. Summary of PEM-DEFC performance

Catalyst	Method of synthesis	Operating Conditions	Power ($mW\ cm^{-2}$)	Ref.
Pt ₇₅ Sn ₂₅	Formic Acid	P _{O2} = 3 bar; [EtOH] = 1.0 mol L ⁻¹ ; T = 90 °C	20	[51]
Pt ₅₀ Sn ₅₀	Polyol	P _{O2} = 2 bar; [EtOH] = 1.0 mol L ⁻¹ ; T = 90 °C	55	[39]
Pt ₈₀ Sn ₂₀	Pechini	P _{O2} = 3 bar; [EtOH] = 2.0 mol L ⁻¹ ; T = 90 °C	37	[52]
Pt ₅₀ Ru ₅₀	Polyol	P _{O2} = 2 bar; [EtOH] = 1.0 mol L ⁻¹ ; T = 90 °C	45	[39]
Pt ₅₂ Ru ₄₈	Colloid	P _{O2} = 1 bar; [EtOH] = 2.0 mol L ⁻¹ ; T = 80 °C	60	[53]
Pt ₅₀ Ru ₅₀	Citric Acid Reduction	P _{O2} = 2 bar; [EtOH] = 2.0 mol L ⁻¹ ; T = 90 °C	20	[54]
Pt ₈₅ Sn ₈ W ₇	Pechini	P _{O2} = 3 bar; [EtOH] = 2.0 mol L ⁻¹ ;	33	[44]

$T = 90\text{ }^{\circ}\text{C}$				
$\text{Pt}_{86}\text{Sn}_{10}\text{Ru}_4$	Bönnemann	$P_{\text{O}_2} = 3\text{ bar}; [\text{EtOH}] = 2.0\text{ mol L}^{-1};$ $T = 80\text{ }^{\circ}\text{C}$	50	[4]
$\text{Pt}_{50}\text{Sn}_{40}\text{Rh}_{10}$	Alcohol Reduction	$P_{\text{O}_2} = 2\text{ bar}; [\text{EtOH}] = 2.0\text{ mol L}^{-1};$ $T = 100\text{ }^{\circ}\text{C}$	42	[16]
$\text{Pt}_1\text{Ru}_1\text{W}_1$	Ethylene glycol Reduction	$P_{\text{O}_2} = 0.2\text{ MPa}; [\text{EtOH}] = 1.0\text{ mol}$ $\text{L}^{-1}; T = 90\text{ }^{\circ}\text{C}$	38	[55]
$\text{Pt}_{79}\text{Sn}_{15}\text{Fe}_{06}$	NaBH_4	$P_{\text{O}_2} = 3\text{ bar}; [\text{EtOH}] = 2.0\text{ mol L}^{-1};$ $T = 80\text{ }^{\circ}\text{C}$	50	this work
$\text{Pt}_{79}\text{Sn}_{19}\text{Ni}_{02}$	NaBH_4	$P_{\text{O}_2} = 3\text{ bar}; [\text{EtOH}] = 2.0\text{ mol L}^{-1};$ $T = 80\text{ }^{\circ}\text{C}$	43	this work
$\text{Pt}_{69}\text{Sn}_{21}\text{Pd}_{10}$	NaBH_4	$P_{\text{O}_2} = 3\text{ bar}; [\text{EtOH}] = 2.0\text{ mol L}^{-1};$ $T = 80\text{ }^{\circ}\text{C}$	43	this work
$\text{Pt}_{71}\text{Sn}_{14}\text{Ru}_{15}$	NaBH_4	$P_{\text{O}_2} = 3\text{ bar}; [\text{EtOH}] = 2.0\text{ mol L}^{-1};$ $T = 80\text{ }^{\circ}\text{C}$	30	this work

Figure 1

Figure 2

Figure 3

Figure 4A

Figure 4B

Figure 5

Figure 6

Figure 7

Figure 8A

Figure 8B