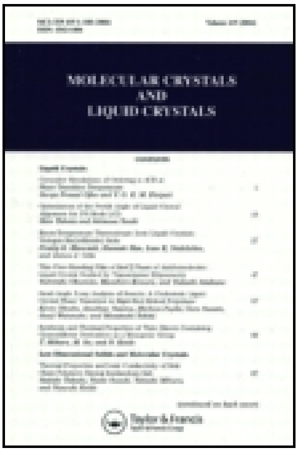

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Characterization of Pt Catalysts for PEM Fuel Cells

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Carbon-supported platinum (Pt\C) was combined with Ru metal or the transition metal oxide NiO, or both NiO and Co_3O_4 to obtain binary and ternary catalyst mixtures respectively. The electrochemical performance of these electrocatalysts for the hydrogen oxidation reaction was investigated using cyclic voltammetry in an in-house three electrode half cell. The physical characterization of the electrode catalysts was analyzed by scanning electron microscopy, energy dispersive X-ray analysis and Brunner-Emmet-Teller adsorption analysis. It was found that it did not matter if NiO was used on its own as an additive or in conjunction with Co_3O_4 in a mixture; the electrical activity improved notably when compared to pure Pt or Pt (40%)\C used in the absence of NiO. The overall metal loading was 0.3 mg.cm^{-2} for both.

Keywords Electrocatalysts; PEM fuel cell; platinum binary mixtures

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) offer a highly attractive alternative energy source because of their ability to produce high energy densities at low-operating temperatures under environmentally friendly conditions. The interest in utilizing this technology has grown substantially over recent years with a considerable move by researchers to adequately solve the various challenges that still hinder its commercialization [1,2].

These challenges mainly exist around the increase in performance at a lowered cost in respect to Pt electrocatalysts by introducing base metals such as (Ni, Co, and Mn), and by improving the reaction kinetics of the electrochemical reactions [3,4].

The energy conversion efficiency of PEM fuel cells is dependent on the activity of the catalyst used for both the anode and cathode reactions. Early PEMFCs used Pt black [5] as the sole catalyst and exhibited excellent performance at a high cost with high metal loading. This was improved considerably by supporting the Pt catalysts on high surface area carbon black without any performance loses [6]. This innovation has brought PEMFCs to the verge of commercialization. While this represented a major development, there is still a drive to further reduce the Pt loading and thereby reduce costs.

Pt has been combined with various base metals such as Cr, Fe, Co, Ni, Cu, Ru, Rh, Pd, Sn, etc. [7] as well as transition metal oxides such as TiO_2, Co_3O_4, NiO, SnO_2, ZnO and CeO_2 in an attempt to resolve the high cost associated when only pure Pt is used [8].

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These mixtures have been created by alloying procedures using in-situ fuel cell analysis and ex-situ characterization has not been thoroughly studied.

The high cost of catalyst powders and membrane material and the direct evaluation of their electro-activity in a complete fuel cell can be both time consuming and expensive, and are therefore not feasible for the evaluation of the catalyst activity of new materials. In this study half cell testing was utilized to characterize the anodic catalysts used in a fuel cell in order to give a better understanding at how a particular catalyst could behave once assembled into a complete single fuel cell.

Cyclic voltammetry (CV) is a highly versatile technique and has frequently been used to estimate the electrochemical surface area (EAS) of Pt-based catalysts by adsorption of atomic hydrogen in acidic media [9]. This will provide a clear indication of the catalyst performance towards the hydrogen oxidation reaction (HOR) at the anode, as well as the oxygen reduction reaction (ORR) at the cathode. The morphology and elemental composition of the gas diffusion electrode (GDE) surface may then be determined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis, together with X-ray fluorescence (XRF), to establish what the condition of the membrane electrode assembly (MEA) in a fuel cell would be.

In this study, binary mixtures comprising of Pt/C with Ru metal and metal oxide, NiO, in ratios ranging from 4:1 to 1:4, as well as ternary mixtures using NiO and Co_3O_4 were prepared and sprayed onto the gas diffuse electrode (GDE) surface and evaluated as both anode and cathode electrocatalysts in order to obtain compositions with high catalytic activity at a reduced cost. These catalysts were compared to commercially available Pt black and Pt/C catalysts. Cyclic voltammetry (CV) was used to evaluate the electrochemical surface area (ECSA) from the hydrogen adsorption peaks, while further characterization was done by SEM\EDX.

Experimental

Materials Used

Platinum black (99.9%, FC grade) was obtained from Sigma Aldrich (Germany). Pt/C black (40 wt% Pt supported on Vulcan XC-72 carbon, FC grade), PtRu black (Pt 50%: Ru 50%) ruthenium black (99.9%, FC grade) and nafion (5% wt, alcoholic solution) was obtained from Alfa Aesar. Nickel(II) oxide was obtained from Judex Lab Reagent and Co(II, III) oxide from Fluka. The carbon paper and carbon cloth was obtained from The Fuel Cell Store (USA).

Preparation of Catalyst Layer

A known amount of catalyst powder was weighed and placed in a vial to obtain a 0.3 mg Pt cm^{-2} loading. In the case of the binary and ternary catalysts, a combined Pt-M loading of 0.3 $mg.cm^{-2}$ was used; where M = Ru, NiO or NiO + Co_3O_4. A drop of H_2O (Millipore), 0.3 ml of Nafion solution and 1.0 ml of ethanol was added in this order. This was placed in an ultrasonic bath for 1 h at 30°C with intermittent swirling of the vial every 15 min to obtain the catalyst ink slurry.

The catalyst ink was deposited onto a gas diffusion electrode (carbon paper) by spraying at 70°C using an air brush. The solvent was allowed to evaporate before the next layer was

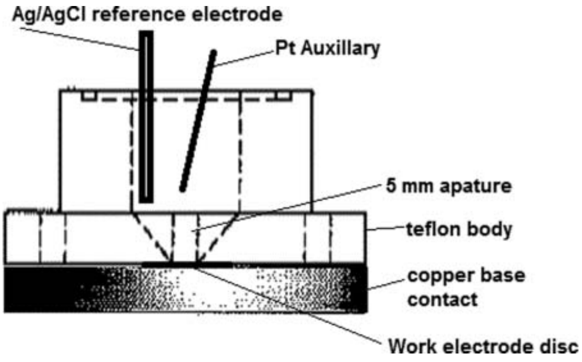

Figure 1. Three-electrode cell used for the half-cell test analysis.

sprayed. The carbon paper was weighed before and after spraying to ensure that the correct catalyst loading was achieved. The electrode was finally dried overnight at 80°C.

Electrochemical Measurements

Cyclic voltammetry was done to determine the electrochemical performance of the catalysts for both the anodic and cathodic potentials. A three-electrode method using an in-house test cell for half-cell analysis was employed (Fig. 1), with the prepared gas diffusion electrode as the working electrode. The cell was purged with nitrogen for 10 min before the measurements were started. Measurements were done against a Ag|AgCl (0.1 M KCl) reference electrode, a Pt-wire electrode as the counter electrode, at scan rates of 50–400 mV/s in 0.5 M H_2SO_4, between the potential limits of the hydrogen evolution reaction. All voltammograms were carried out at room temperature using an Epsilon System and all potentials were referred to relative hydrogen electrode (RHE) in this study.

Scanning Electron Microscopy and X-ray Diffraction Analysis

The surface morphology and elemental composition of the prepared gas diffuse electrodes were observed by scanning electron microscopy (SEM) using a Joel SEM 6380 and the elemental composition determined by energy dispersive X-ray (EDX) analysis respectively. Some of the samples were subjected to EDX elemental scan mapping across the surface of the sample. X-ray powder diffraction (PXRD) studies were done of the pure catalyst starting material in order to determine the correct phase content of the material and to determine the average crystallite size from the full width at half maximum main peak intensity (FWHM) using the Scherer equation. The analysis was done on a Bruker D8 Advance with Cu radiation. Standard Bragg Brentano geometry was used with a Ni filter at the detector.

Results and Discussion

Physical Properties of Catalyst Powders

The crystallite size of each metal powder used was calculated using the Scherer equation:

$$t = K\lambda/B(\cos\theta) \tag{1}$$

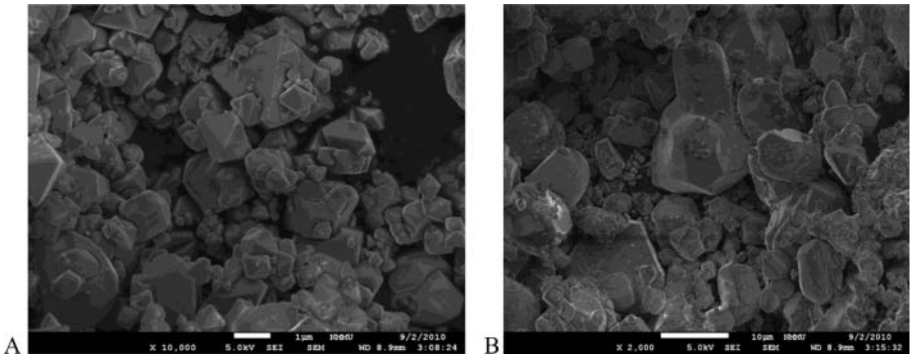

Figure 2. SEM images of a) NiO and b) Co_3O_4 indicating their wide particle distribution range.

where t = average dimensions of crystallites, K = Scherrer constant or shape constant (assumed to be 1), λ = wavelength of X-ray (154.18 pm) and B = FWHMof the reflection located at 2θ. The crystallite sizes as determined by PXRD of the metal oxides showed a relatively broad crystallite size distribution. It must be remembered that the crystallite size that is determined by the Scherer equation is limited to nano particles, where the results of larger particles ($>0.1\ \mu$m) the results are rather an indication of the micro crystallites that occur within the larger grains. The SEM images shown in Fig. 2 indicated that the metal oxides had a relatively wider particle size distribution of between 1 to 10 μm.

Cyclic Voltammetry Studies

The electrochemical performance of catalyst materials can be indirectly studied by comparing the voltammetric behaviour of Pt black and Pt/C (40%) (Fig. 3). From the anodic scan the hydrogen desorption peaks of −0.25 to 0.1 V vs. AglAgCl as reference electrode were observed and the surface area was calculated from the peaks. It is known that by supporting Pt particles on carbon, the active catalytic surface area increases and this was evident from the increased hydrogen adsorption of Pt/C when compared to Pt black. By supporting the catalyst on a carbon paper/cloth electrode surface, the absorption and desorption peaks on the cyclic voltammetry becomes more prominent where the catalysts showed good stability and durability after 20 scans on this 5mm electrode surface.

Figures 4 and 5 compared the voltammetric behaviour of the binary mixtures comprised of $Pt_{50}M_{50}$ and $Pt_{20}M_{80}$ respectively; where M = Ni or Ru. Figure 6 described the voltammetric behaviour of the ternary mixture, $Pt_{33}Ni_{33}Co_{33}$ and was compared to that of Pt/C.

In comparing the various scans in Fig. 4 it can be observed that $Pt_{50}Ni_{50}$ mixtures give a better electrochemical surface area in comparison to Pt black and $Pt_{50}Ru_{50}$ mixtures. In Fig. 5, it can clearly be observed that the electrochemical surface are drop considerable for the $Pt_{20}Ni_{80}$ mixture compared to Pt black. This is due to the instability of Ni (111) at this pH = 2 range. In Fig. 6, it can be seen that when a ternary mixture was prepared, it gave a far worst outcome regarding the electrochemical active surface area, which indicates that the PtNiCo mixture gave only an activity towards the Pt (111) surface, while both the Ni and Co are dissolved into the electrolyte medium.

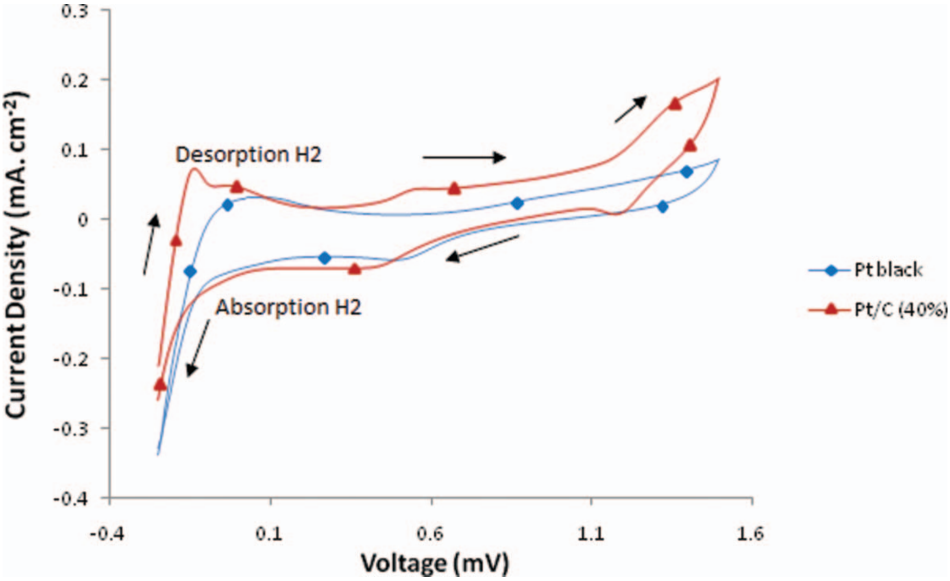

Figure 3. Cyclic voltammograms for Pt black and Pt/C at 25°C vs. Ag|AgCl in 0.5 M H_2SO_4. The potential scan was 150 mV/s.

The electrochemical active surface area was calculated by using the following calculation:

$$S_{ECSA}(m^2/g) = \frac{\text{Charge area}\,(\mu C/cm^2)}{[210\,(\mu\, C/cm^2)\ \times\ \text{catalyst loading}\,(mg/cm^2)} \tag{2}$$

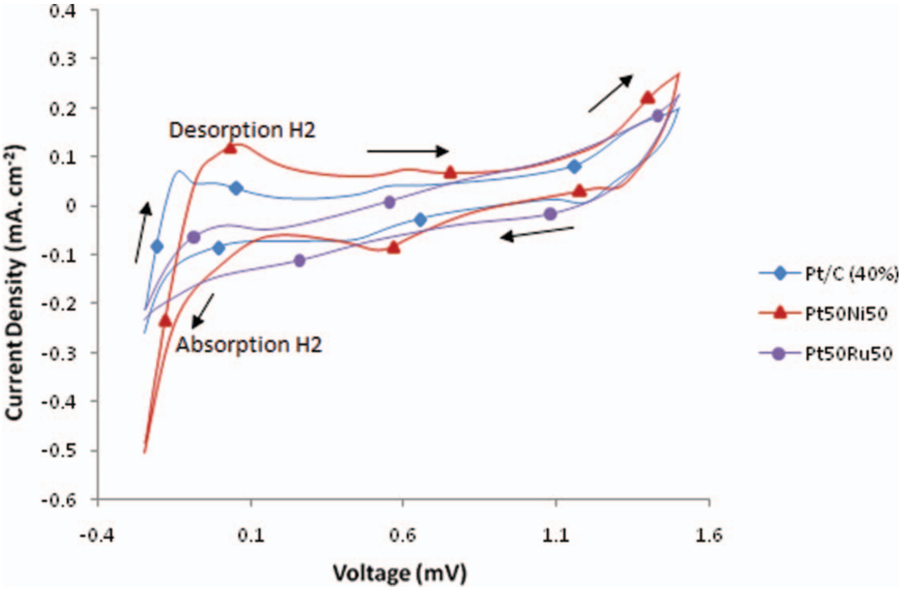

Figure 4. Cyclic voltammograms for Pt/C and $Pt_{50}M_{50}$ at 25°C vs. Ag|AgCl in 0.5 M H_2SO_4. The potential scan was 150 mV/s.

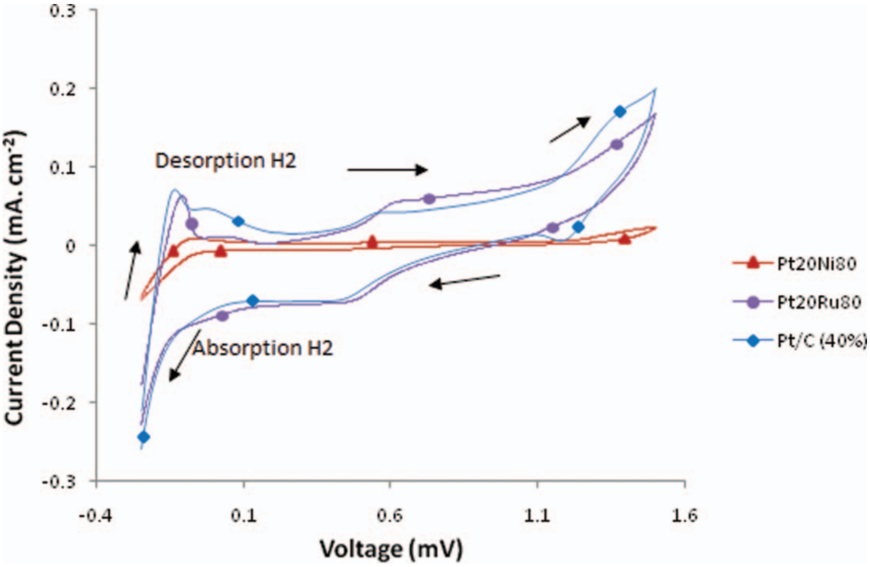

Figure 5. Cyclic voltammograms for Pt/C and $Pt_{20}M_{80}$ at 25°C vs. Ag|AgCl in 0.5 M H_2SO_4. The potential scan was 150 mV/s.

Where S_{ECSA} is the active surface area of the catalyst and 210 is a factor that considers the ratio or the electrons to the active surface area ($\mu C/cm^2$) [10–12].

The results are summarized together with the Pt loading of each catalyst in Table 1. They showed that for the various mixtures prepared, the mixture with $Pt_{20}M_{80}$ (M = Ni,

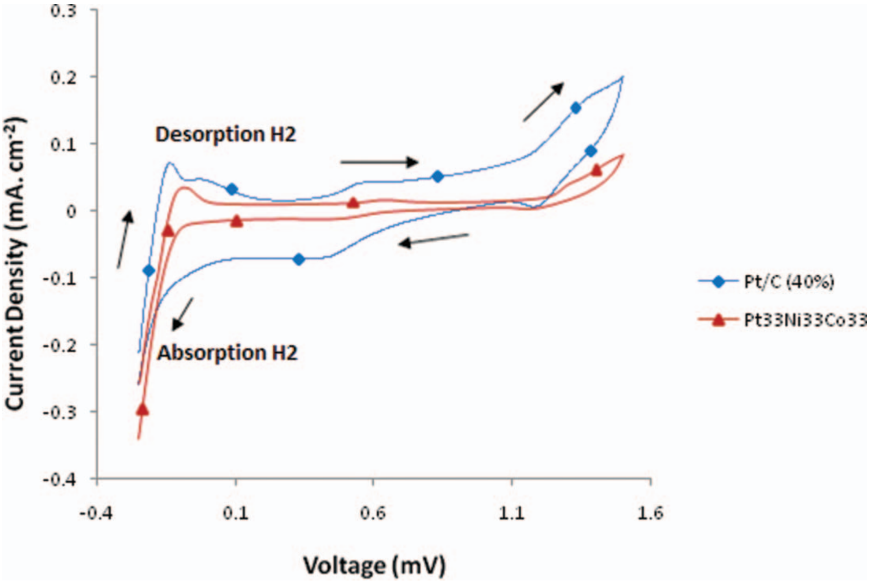

Figure 6. Cyclic voltammograms for Pt/C and $Pt_{33}Ni_{33}Co_{33}$ at 25°C vs. Ag|AgCl in 0.5 M H_2SO_4. The potential scan was 150 mV/s.

Table 1. H_2 adsorption measurements and ECSA calculations for various catalyst mixtures. Scan rate was 150 mV/s

Sample	Pt Loading (mg/cm^2)	H_2 Adsorption (QH) mC	Electrochemical Surface Area S_{ECSA} (m^{2}g^{-1})
Pt black	0.06	6.16	49.83
Pt/C (40%)	0.06	6.78	54.85
$Pt_{50}Ni_{50}$	0.30	2.77	44.78
$Pt_{50}Ru_{50}$	0.30	2.82	45.61
$Pt_{20}Ni_{80}$	0.10	2.59	104.7
$Pt_{20}Ru_{80}$	0.15	1.85	74.98
$Pt_{33}Ni_{33}Co_{33}$	0.15	1.89	45.86
$Pt_{20}Ni_{60}Co_{20}$	0.15	0.47	7.59
$Pt_{20}Ni_{40}Co_{40}$	0.15	0.69	11.13

Ru) was found to have a higher ECSA when compared to the plain Pt/C, indicating that these could have good potential for better catalytic activity in PEM fuel cells. The results also showed that a possibility for a ternary mixture exists, with metals in equal proportions, to have activity comparable to that of Pt/C and Pt black. This could lead to a substantially reduced Pt loading without any major loses in electrocatalytic performance.

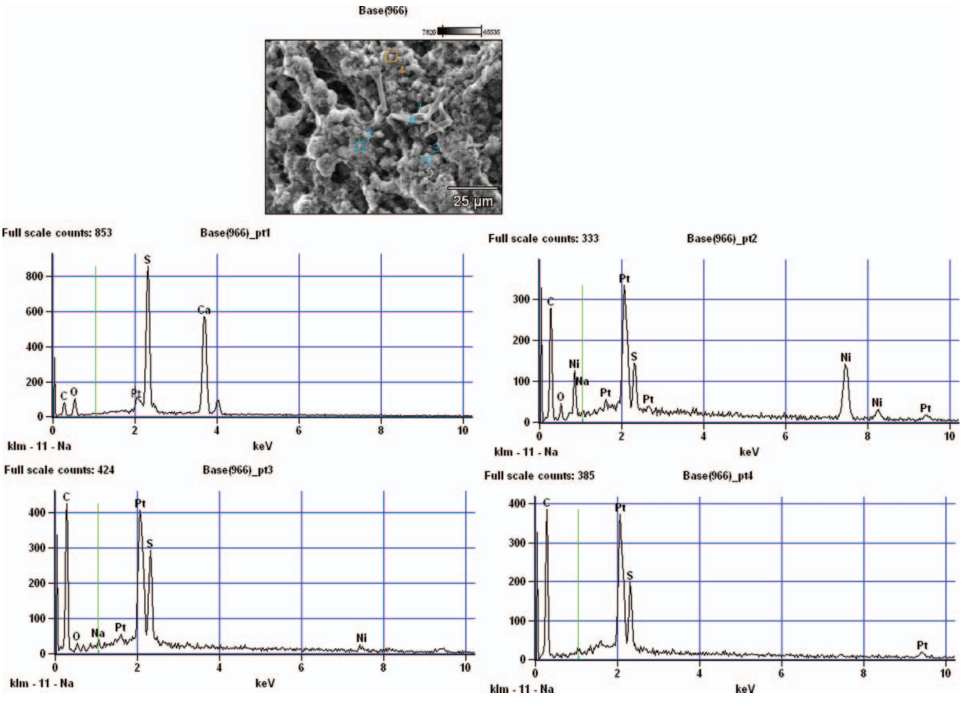

Figure 7. a) SEM micrograph of GDE coated with $Pt_{50}Ni_{50}$ showing spots where EDX analysis was performance; b) EDX spectra of the $Pt_{50}Ni_{50}$ deposited gas diffuse electrode taken at various spots showing the presence of Pt and Ni, as well as C and S.

SEM/EDX and Elemental Mapping of Catalyst Layer Electrode Surface

The electrodes prepared showed good adherence to the carbon surface, with both Pt and Ni in conjunction with carbon (catalyst support) and sulfur (from Nafion), indicating that the Nafion acted as a binding agent. (Fig. 7)

The EDX analysis done from different sections of the catalyst sample $Pt_{50}Ni_{50}$ indicated four different sections as shown in Fig. 7b. The individual point analysis showed that there were different atomic percentages of Pt and Ni, indicating that the elements are not necessarily distributed uniformly on the support surface and that there could be considerable segregation of the metals. While the EDX of section 1 shows only presence of Pt, there are also cross sections where both Pt and Ni have been found in close proximity. The dissolution of the Ni metal into the electrolyte medium is possible and can be explained by considering the Pourbaix diagrams of NiO where that the Ni_{111} is only stable at pH above 8 [13–14].

Elemental mapping of the areas as observed in Fig. 8 showed the overall distribution of the catalyst across the GDE surface. Each of the concerning elements namely Pt and Ni, are well distributed on the carbon support and thus the spraying deposition method was found to be effective. The even distribution, which was critical for the performance of fuel cell catalysts where limited agglomerations of the Ni particles were observed, may also hinder its performance.

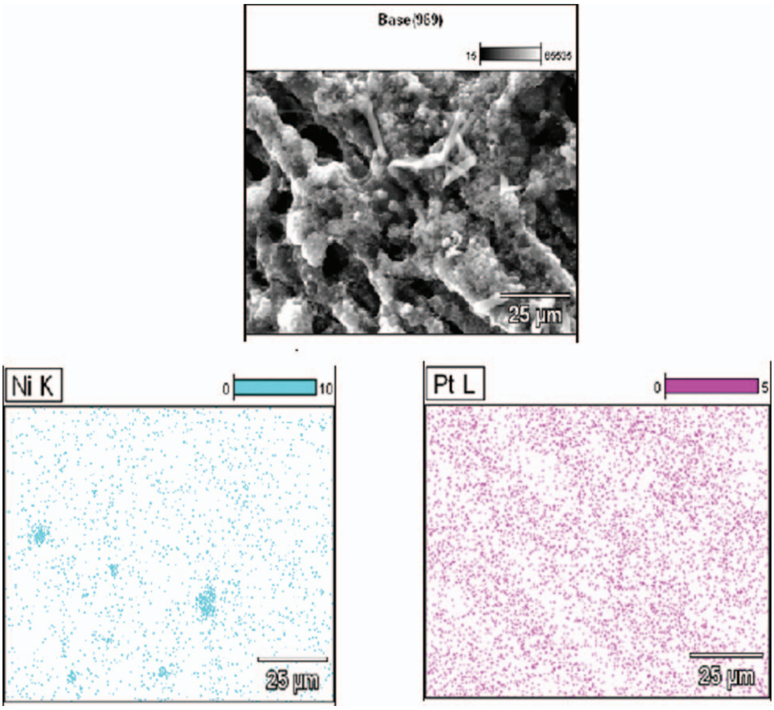

Figure 8. Mapping spectra of the $Pt_{50}Ni_{50}$ deposited gas diffuse electrode, showing the elemental distribution of Pt and Ni.

Conclusion

In this study, possible catalyst for PEM fuel cell electrodes were studied and characterized. The half cell reactions for Pt (black) and Pt/C on their own and with metal oxides such as NiO and Co (II,III) oxide mixtures, were investigated by means of cyclic voltammetry. The physical characterizations were done by means of SEM imaging, BET and XRD analysis. The ECSA showed a large surface area to gram for Pt / NiO compared to Pt black or Pt/C catalysts. ECSA was determined by cyclic voltammetry Pt black gave a value of 42 m^2/g with PtNi give a ECSA of 96 m^2/g.

Further research in this group will be to produce an alloy mixture between Pt and Ni or Co, or even a mixture of Co and Ni to Pt to study its effect on durability and performance in a fuel cell.

Acknowledgments

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