

An oxidation-resistant indium tin oxide catalyst support for proton exchange membrane fuel cells

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Abstract

The oxidation of carbon catalyst supports causes degradation in catalyst performance in proton exchange membrane fuel cells (PEMFCs). Indium tin oxide (ITO) is considered as a candidate for an alternative catalyst support. The electrochemical stability of ITO was studied by use of a rotating disk electrode (RDE). Oxidation cycles between +0.6 and +1.8 V were applied to ITO supporting a Pt catalyst. Cyclic voltammograms (CVs) both before and after the oxidation cycles were obtained for Pt on ITO, Hispec 4000 (a commercially available catalyst), and 40 wt.% Pt dispersed in-house on Vulcan XC-72R. Pt on ITO showed significantly better electrochemical stability, as determined by the relative change in electrochemically active surface area after cycling. Hydrogen desorption peaks in the CVs existed even after 100 cycles from 0.6 to 1.8 V for Pt on ITO. On the other hand, most of the active surface area was lost after 100 cycles of the Hispec 4000 catalyst. The 40 wt.% Pt on Vulcan made in-house also lost most of its active area after only 50 cycles. Pt on ITO was significantly more electrochemically stable than both Hispec 4000 and Pt on Vulcan XC-72R. In this study, it was found that the Pt on ITO had average crystallite sizes of 13 nm for Pt and 38 nm for ITO. Pt on ITO showed extremely high thermal stability, with only ~1 wt.% loss of material for ITO versus ~57 wt.% for Hispec 4000 on heating to 1000 °C. The TEM data show Pt clusters dispersed on small crystalline ITO particles. The SEM data show octahedral shaped ITO particles supporting Pt. © 2006 Published by Elsevier B.V.

Keywords: Catalyst support; Oxidation; Indium tin oxide; Ebonex; Carbon; Proton exchange membrane fuel cells

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical energy conversion devices that electrochemically react hydrogen and oxygen to produce electricity. They can be used for power generation in portable, stationary, and transportation applications. The main component of the PEMFC is the membrane electrode assembly (MEA). Development of MEAs with longer lifetimes and higher power efficiencies and made from the lowest cost components is ongoing. Catalyst support corrosion has been observed as a serious problem that leads to extensive MEA degradation [1], thus limiting MEA lifetimes.

In the literature, carbon catalyst support corrosion has been predominantly observed in phosphoric acid fuel cells (PAFC) [1]. Although the operating temperature range of PEMFCs is

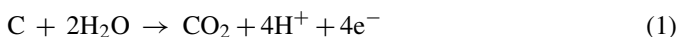
lower than that of PAFCs, degradation in performance due to catalyst support corrosion has been observed in PEMFCs during duty cycling [1]. The metal catalysts in a PEMFC are typically impregnated into the porous structure of a carbon support material. These support materials can be chemically or physically activated carbons, carbon blacks, and graphitised carbons. The catalyst support serves several functions:

- To provide high surface area over which small metallic particles can be dispersed and stabilized.
- To allow facile mass transport of reactants and products to and from the active sites.
- To provide electronic conductivity within the catalyst layer.
- To provide thermal conductivity within the catalyst layer.

Electrochemical oxidation of the carbon supports produces microstructural degradation and surface chemical changes, which generally leads to lost catalyst active surface area. It is

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known that carbon oxidizes in aqueous solution by the following reaction [2]:



The standard electrode potential for this reaction at 25 °C is 0.207 V versus SHE. Carbon is thermodynamically unstable above this potential and is therefore susceptible to oxidation in typical cathodic environments. Pt also plays a role in accelerating the carbon corrosion. Results from differential electrochemical mass spectroscopy (DEMS) performed on Pt supported on carbon obtained by Roen et al. [3] showed that CO₂ emission was directly proportional to the Pt surface area supported on carbon. It has therefore been concluded that Pt catalyzes the electrochemical oxidation of carbon.

Several methods for stabilizing the carbon supports against corrosion have been reported including graphitisation, boron and phosphorous doping, and forming nanotubes or aerogels [4–7]. However, these methods do not prevent oxidation, but rather simply decrease the rate. The use of conductive zeolite materials, conducting polymer/proton exchange polymer composites, and carbides have also been studied [8–10]. The aluminosilicate based zeolite materials alone are not conductive and usually carbon is added to these materials to make them conductive [8]. Since carbon corrosion is observed in PEMFCs this support material may not be stable under PEMFC conditions. Commercially available carbides usually have low surface areas as they are used extensively for non-fuel cell applications [11]. Therefore, the surface areas of carbides need to be enhanced before they can be used as high performing and electrochemically stable supports in PEMFCs.

Conducting oxides are emerging candidates for oxidation resistant catalyst supports. Sub-stoichiometric compositions of the general formula $\text{T}_n\text{O}_{2n-1}$ (Magneli phase, where n is between 4 and 10) exist for the titanium-oxygen system, and Ti_4O_7 in particular exhibits a high electrical conductivity of 1000 S cm^{-1} at room temperature, compared to graphitized carbon with a conductivity of 727 S cm^{-1} [12]. Chen et al. [13] studied three oxide supports: Ebonex (Atraverda Ltd., U.K.), phase-pure microcrystalline Ti_4O_7 , and a doped rutile compound, $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$. Ebonex is an electronically conducting ceramic consisting of several suboxides of titanium (Ti_4O_7 and other phases). Ti^{3+} ions enhance the conductivity in the Magneli phases of titania. The Ti^{3+} ions can be created by forming oxygen vacancies by heating TiO_2 in a reducing atmosphere or by introducing appropriate donor dopants, *e.g.*, Nb or F. Both Ebonex and Ti_4O_7 can be oxidized to resistive TiO_2 under cathodic conditions, but $\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_2$ remains both thermally and electrochemically stable. Polarization data showed that Ebonex and Ti_4O_7 are oxidized to non-conductive TiO_2 at the catalyst/support/electrolyte three-phase interface after extensive polarization at the positive potentials of the oxygen electrode [13]. The work by Chen et al. [13] indicates that although conductive oxides can be created either by formation of a non-stoichiometric oxide or by doping, doping is the preferred method for enhancing electronic conductivity and maintaining it in oxidizing environments.

Indium tin oxide (ITO) is a commercially available material often used as a transparent conducting oxide (TCO) for smart windows. It is the intent of this work to study the electrochemical stability of this potential non-carbon catalyst support. Both thermal and electrochemical stability of Pt supported on ITO are studied and compared with those of commercially available catalyst Hispec 4000, and of Pt deposited on Vulcan XC-7R using the same method used to deposit the Pt on ITO.

2. Experimental procedure

We have investigated the suitability of ITO, a material with electrical conductivity of 1000 S cm^{-1} [12], for use as a catalyst support by evaluating the electrochemical stability of ITO in ex situ tests. ITO is a tin (Sn (IV))-doped, In_2O_3 -based n-type semiconductor. Pt was deposited on ITO, and both the thermal and electrochemical stability were compared with that of commercially available catalyst Hispec 4000 (Johnson Matthey, 40% Pt deposited on Vulcan XC-72R (Cabot)). Vulcan XC-72R is a commercially available carbon used extensively as a support for PEMFCs. Commercially available ITO (Nanophase) was used in this study. Thermogravimetric analysis (TGA), X-ray diffraction (XRD), rotating disc electrode (RDE) studies, and transmission and scanning electron microscopy (TEM and SEM) were used to characterize the catalyst support material. Since Hispec 4000 may be manufactured differently than the Pt dispersion method used in this study, we also dispersed 40 wt.% Pt on Vulcan XC-72R using the same method as that used to disperse 40 wt.% Pt on ITO to allow a more direct comparison of the support materials to be made.

The Pt was added to Vulcan XC-72R and commercially available ITO (Nanophase) as follows: 3.444 g NaHCO_3 was dissolved in 200 ml of H_2O in a 500 ml round bottom flask. To this solution 0.6 g of the catalyst support was added. The mixture was refluxed for several hours to ensure complete wetting of the support. Using an addition funnel, 1 g H_2PtCl_6 dissolved in 60 ml of H_2O was added drop-wise over several minutes. The mixture was again allowed to reflux for 2 h. Seven hundred and eighty microliters methanol (HCHO) solution (37%) in 7.8 ml H_2O was added by addition funnel over approximately 1 min. The mixture was allowed to react and reflux overnight before filtering, washing, drying and grinding of the solid.

Thermogravimetric analysis (TGA) was used to determine the thermal stability of the conventional carbon support and of ITO (Nanophase) support materials to oxidation in air flowing at 40 ml min^{-1} . The temperature was ramped from room temperature to 50 °C at 2 °C min^{-1} . The sample was then held at 50 °C for 5 min to allow time for water removal. The sample was then ramped from 50 to 1000 °C at 2 °C min^{-1} . The same procedure was used for the catalysts containing 40 wt.% Pt on Vulcan XC-72R and for commercially available ITO with and without added Pt. The data were analyzed by plotting the derivative of the mass as a function of sample temperature (dm/dT) to more readily identify the onset of oxidation. Normalized weight loss was plotted for each material versus temperature to determine the thermal stability of the supports under investigation.

X-ray diffraction (XRD) was used to determine the presence of crystalline Pt on the ITO supports and the average crystallite sizes. Crystallite sizes of the Pt and of the ITO were calculated using the Scherrer equation [14]:

$$t = 0.9 \left(\frac{\lambda}{b} \right) \cos \theta_b,$$

where t is the crystallite size in Å, λ the wavelength (1.5406 Å in this case for Cu K α radiation), b the full-width at half maximum (FWHM) of a peak in the XRD spectrum, and θ_b is the diffraction angle for that peak.

To test the electrochemical stability of the catalyst supports, 20 mg of each supported catalyst was dispersed in 2 ml of glacial ethanoic acid using ultrasound. Using a micropipette, 5 μ l of the suspension was dispensed onto the flat surface of a polished glassy carbon (GC) rotating disc electrode (RDE). The solvent was removed gently with a hot air blower, leaving supported catalyst (50 μ g, \approx 20 μ g Pt) on the disc. Using the same micropipette, 5 μ l of 5% alcoholic NafionTM (DuPont) solution with EW of 1100 was dispensed onto the disc. The solvent was allowed to slowly evaporate in still air in a glass enclosure so that a coherent NafionTM film was cast over the catalyst and the disc. The RDE was then immersed in deoxygenated 0.5 M H₂SO₄ at 30 °C and rotated at 33.33 Hz (2000 rpm). The electrochemical cell comprised a glass working compartment with a water jacket connected to a circulating water bath and two side compartments: one containing a Pt gauze counter electrode connected by a glass frit, and the other containing the reversible hydrogen electrode (RHE) connected by a Luggin capillary.

Based on preliminary voltage cycling experimental results, the oxidation potential chosen for the electrochemical cycling tests was +1.8 V versus RHE. Above +1.8 V, considerable gas was evolved, which separated the catalyst/NafionTM deposit from the disc. At lower potentials, the oxidation was not detectable in a suitable experimental timeframe. The oxidation cycling procedure was as follows. Using an EG&G 263 (PAR, Princeton, NJ) potentiostat with Corrware software (Scribner

Associates), potential steps (oxidation cycles) between +0.6 and +1.8 V were applied. The electrode was held at 0.6 V for 60 s and at 1.8 V for 20 s. A cyclic voltammogram (CV) was recorded between 0.0 and 1.4 V at 100 mV s⁻¹ before the oxidation cycles began and then again after every 10 oxidation cycles, until total of 100 oxidation cycles had been applied. Three separate tests were completed for each sample to observe repeatability, and the average data with limits of error were plotted for the normalized activity.

3. Results and discussion

3.1. TGA results

Fig. 1 shows TGA data for Hispec 4000, Vulcan XC-72R, and Pt deposited in-house on Vulcan XC-72R. The peak at very low temperatures is due to loss of moisture. Hispec 4000, which is more active than the catalyst made in-house (40% Pt on Vulcan XC-72R), starts to thermally oxidize at \sim 300 °C, while the in-house Pt/Vulcan starts to oxidize at \sim 325 °C. Vulcan XC-72R without Pt does not start to oxidize until \sim 700 °C. The thermal oxidation results of Pt supported on Vulcan XC-72R agree with the findings by Roen et al. [3] that Pt catalyzes the oxidation of carbon. Fig. 2 shows the normalized weight loss for several catalyst support materials as a function of temperature. After heating the materials to 1000 °C under air, Vulcan lost 100% of its weight, Hispec 4000 lost 57 wt.%, \sim 40 wt.% Pt on Vulcan lost 55 wt.%, ITO lost 1 wt.%, and Pt/ITO lost 0.7 wt.%. The losses for Hispec 4000 and 40% Pt on Vulcan correspond to a loss of carbon, and the remaining weight corresponds to the Pt metal left in the TGA crucible. This result clearly indicates that the ITO support is thermally stable, in contrast to the other support materials studied.

3.2. X-ray diffraction

The XRD pattern for 40% Pt supported on ITO is shown in Fig. 3. Using the Scherrer equation, the Pt crystallite size was

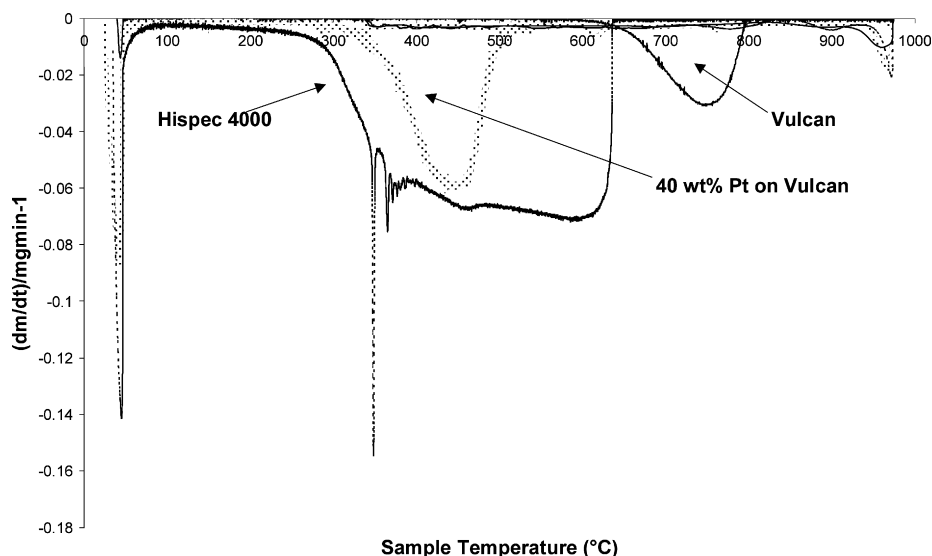


Fig. 1. TGA data for Hispec 4000 and Vulcan; under air at 40 ml min⁻¹, temperature ramped from 50 °C to 1000 °C at 2 °C min⁻¹.

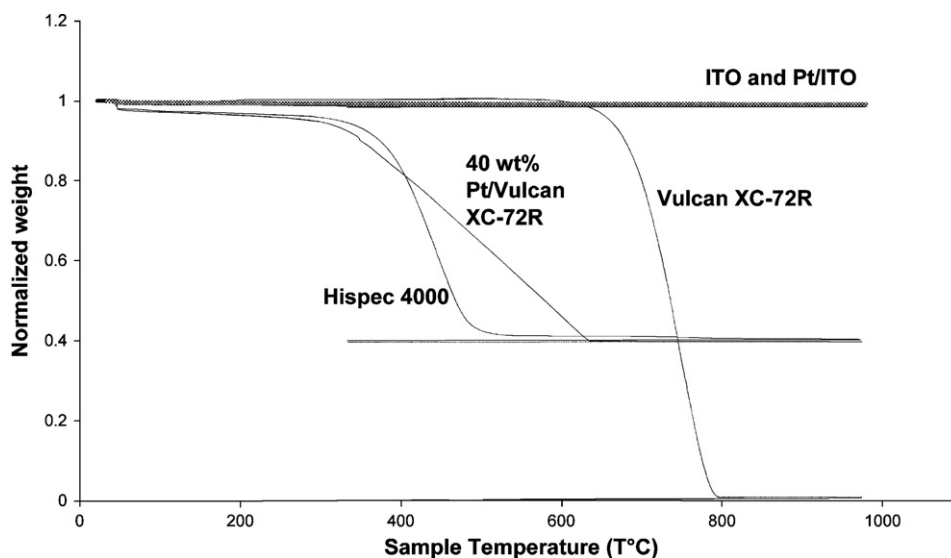


Fig. 2. TGA data for Hispec 4000, Vulcan XC-72R, Pt on Vulcan, Pt on ITO, and ITO; under air at 40 ml min^{-1} , temperature ramped from 50°C to 1000°C at 2°C min^{-1} .

calculated to be 13 nm and that of ITO was 38 nm. Catalyst supports with particle sizes ranging from 50 to 100 nm are typically used in PEMFCs, and Pt supported on carbon with Pt crystallite size ranging from 3 to 8 nm have been reported and are commercially available. The ITO particles used in this study are much smaller than would be required to support a high dispersion of Pt particles. The activity of a well-dispersed catalyst would be higher than that of an agglomerated catalyst with lower surface area. Sol-gel methods can be used in future studies to modify the ITO surface area and Pt crystallite sizes in order to fully optimize the particle size distributions for higher overall catalyst performance.

3.3. Rotating disc electrode

Fig. 4 shows the results of oxidation cycles from +0.6 to +1.8 V for Hispec 4000, Pt/ITO, and Pt on Vulcan. These data were used to calculate the normalized activity for Hispec 4000 and Pt/ITO, shown in Fig. 5. The normalized activity was calcu-

lated by recording the last current point from the data set at 1.8 V just before the current became negative under 0.6 V conditions. These points are marked with arrows as points 1, 2, 3, etc. in Fig. 4. The current at point 1 was taken as the initial current for the normalized activity plots. The current decreased as the catalyst support oxidized, so the currents subsequent to point 1 were normalized to the initial current value, and the curve in Fig. 5 was plotted as the normalized activity versus the cumulative number of oxidation cycles. Comparing Hispec 4000, Pt on ITO, and Pt on Vulcan XC-72R being held at 1.8 V for 20 s per cycle, the stability follows the order of: Pt/ITO \gg Hispec 4000 \approx 40 wt.% Pt on Vulcan. Pt on Vulcan and Hispec 4000 lost most of their activity after 10 cycles. Pt on Vulcan had similar thermal stability and activity loss under oxidation cycles to those of Hispec 4000, indicating that the method used in-house to disperse Pt yields catalyst with similar activity as commercially available Hispec 4000. Pt on ITO after 10 cycles only lost $\sim 25\%$ of its activity, indicating a much more stable support than Vulcan XC-72R. The ITO particle size is lower than that of Vul-

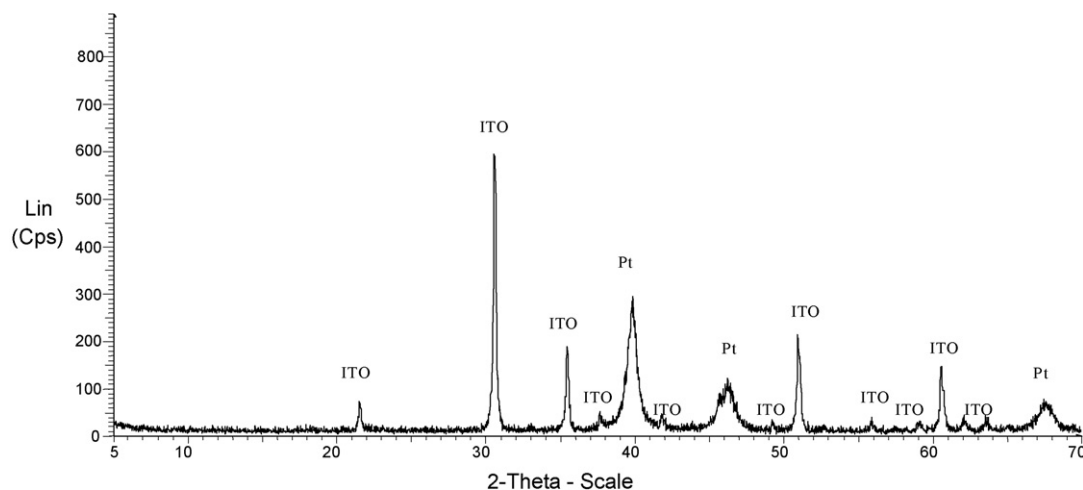


Fig. 3. XRD diffraction pattern for 40% Pt deposited on ITO deposited by NaHCO_3 route.

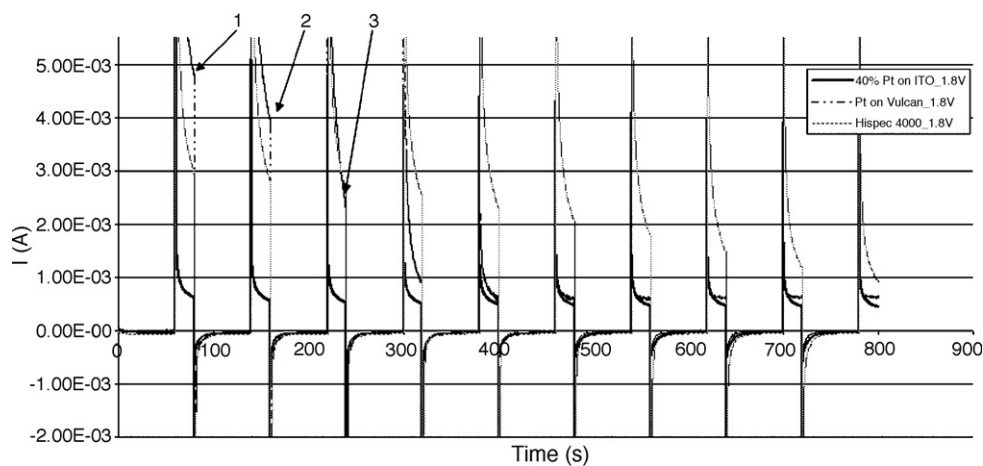


Fig. 4. Oxidation cycles for Hispec 4000, Pt on ITO, and Pt on Vulcan from 0.6 to 1.8 V, held at 1.8 V for 20 s.

can XC-72R; however, by using sol–gel methods, the surface area of ITO can be enhanced and it will be useful to study the activity of ITO with optimized surface area, with catalyst dispersed by similar methods as used in the current study. Cyclic voltammetry was done both initially and after every 10 oxidation cycles from 0.6 to 1.8 V until 100 oxidation cycles were reached. The slight increase in activity at oxidation cycles 11 and 21 for ITO are observed because after 10 cycles, a CV test was performed, which increased the activity just before the start of the next set of oxidation cycles.

Figs. 6 and 7 show the cyclic voltammograms of Pt on ITO and Hispec 4000, respectively, both before and after 100 oxidation cycles. Pt on ITO showed significantly better electrochemical stability, as determined by a lower loss of electrochemically active surface area. This surface area was determined from the area under the hydrogen adsorption curves. Hydrogen adsorption peaks were present for the Pt on ITO even after 100 cycles from 0.6 to 1.8 V. On the other hand, most of active surface area of the Hispec 4000 was lost after 100 cycles. Also, the

Pt reduction peak for Hispec 4000 was observed to shift to lower potentials (0.75–0.55 V), whereas, the Pt reduction peak for Pt supported on ITO did not shift even after 100 cycles. The 40% Pt on Vulcan lost almost all of its active area after only 50 cycles (Fig. 8). The total currents in the cyclic voltammetry tests for ITO supporting Pt were much lower than those for Hispec 4000 because the active surface area of the Pt particles on the ITO is much lower than that in Hispec 4000. Changing the microstructure of the catalyst/support combination in future tests can modify this total activity.

3.4. TEM and high resolution SEM images

Figs. 9 and 10 show the high resolution SEM images for ITO and 40% Pt on ITO, respectively. A mixture of spherical and octahedral structure of ITO crystallites is clearly visible for the ITO sample. Small Pt particles are observed for the 40% Pt on ITO sample in the SEM images.

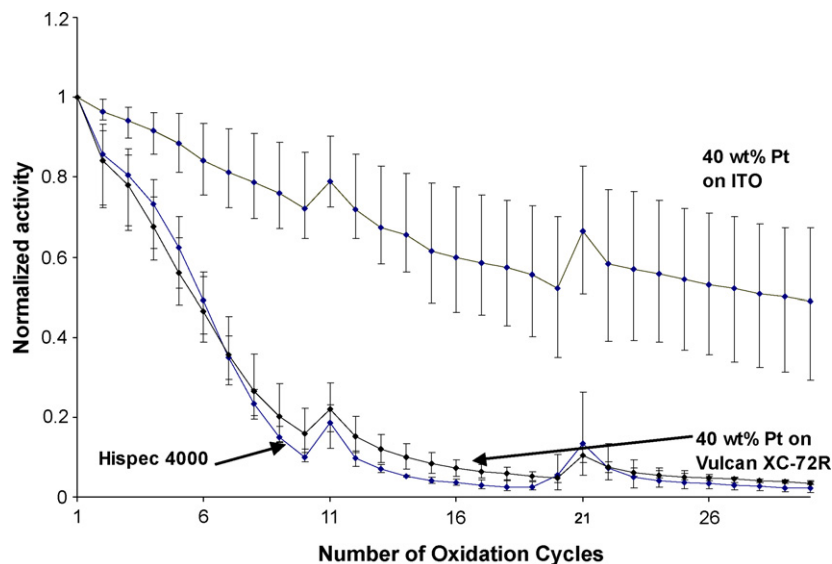


Fig. 5. Normalized activity at different potentials as a result of repeated cycling for different 40 wt.% Pt catalysts. Average of three separate tests and limits of error for each sample are plotted.

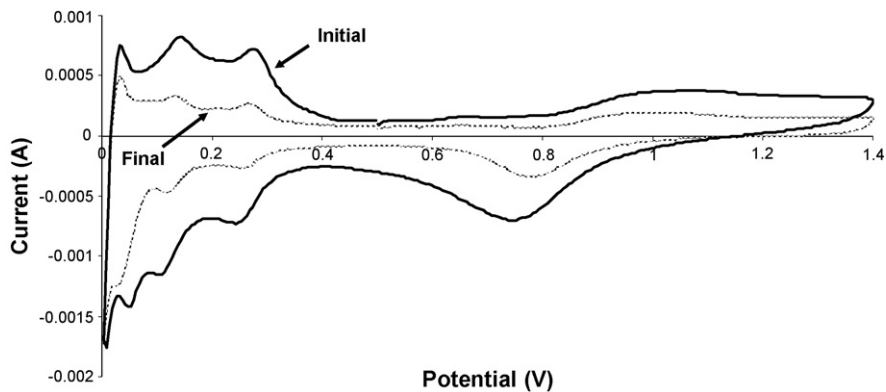


Fig. 6. Cyclic voltammograms (CVs) for 40 wt.% Pt on ITO both before and after oxidation cycles at 1.8 V, 100 oxidation cycles were run. Electrochemical stability with no change in the CV curves is observed from cycle 30 onwards; 0.5 M H₂SO₄, 30 °C, 100 mV/s, 2000 rpm.

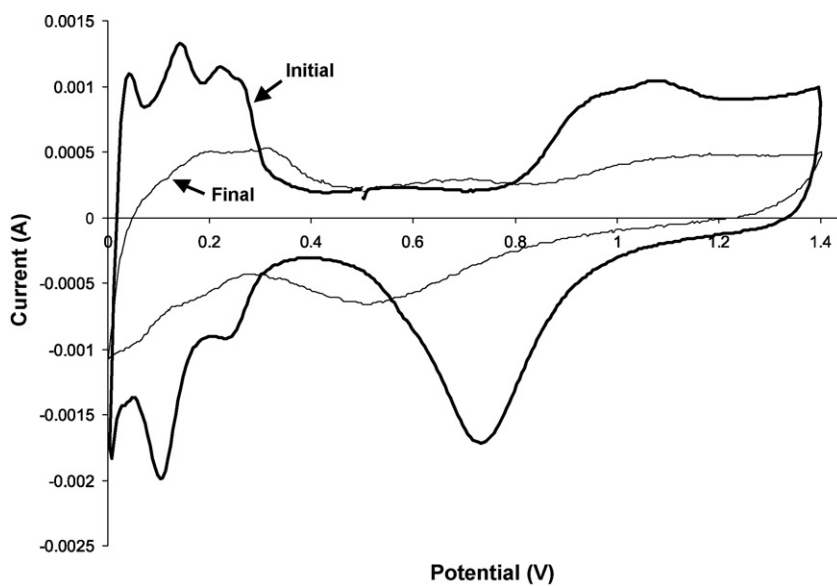


Fig. 7. Cyclic voltammograms for Hispec 4000, both before and after 100 oxidation cycles; 0.5 M H₂SO₄, 30 °C, 100 mV/s, 2000 rpm.

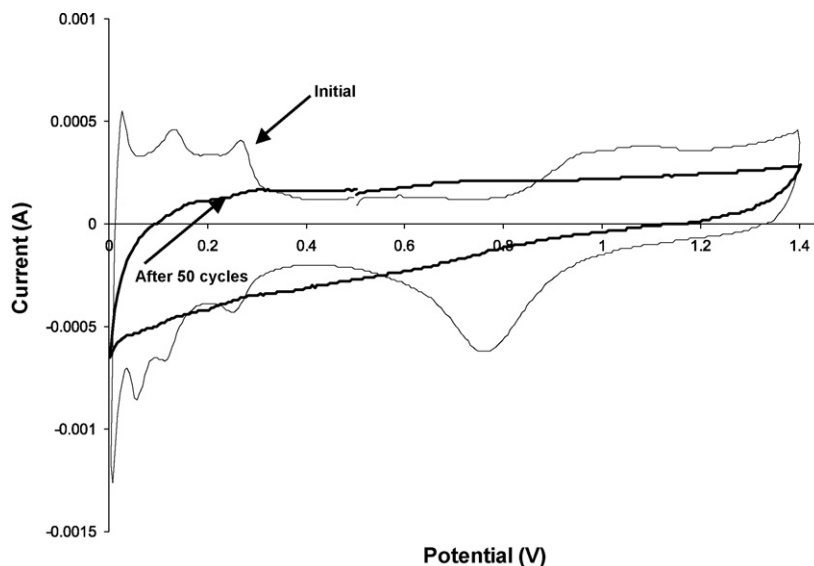


Fig. 8. Cyclic voltammograms for 40 wt.% Pt on Vulcan XC-72R, both before and after 50 oxidation cycles; 0.5 M H₂SO₄, 30 °C, 100 mV/s, 2000 rpm.

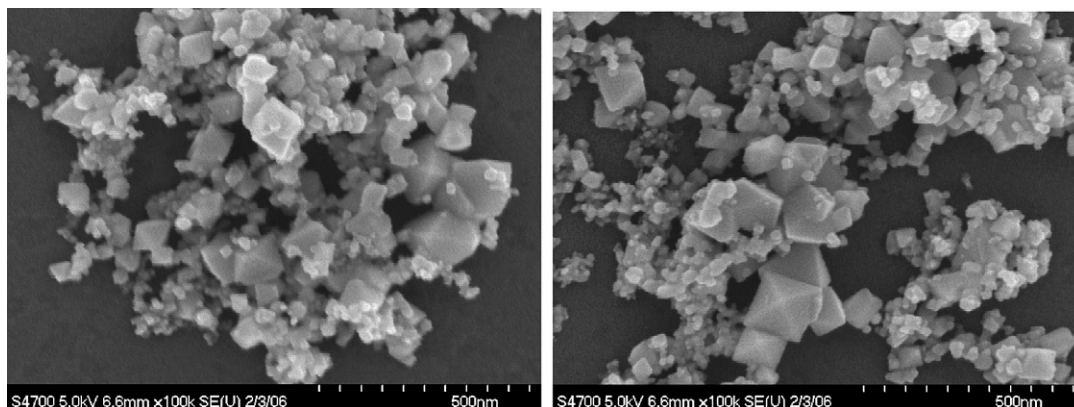


Fig. 9. High resolution SEM images of ITO.

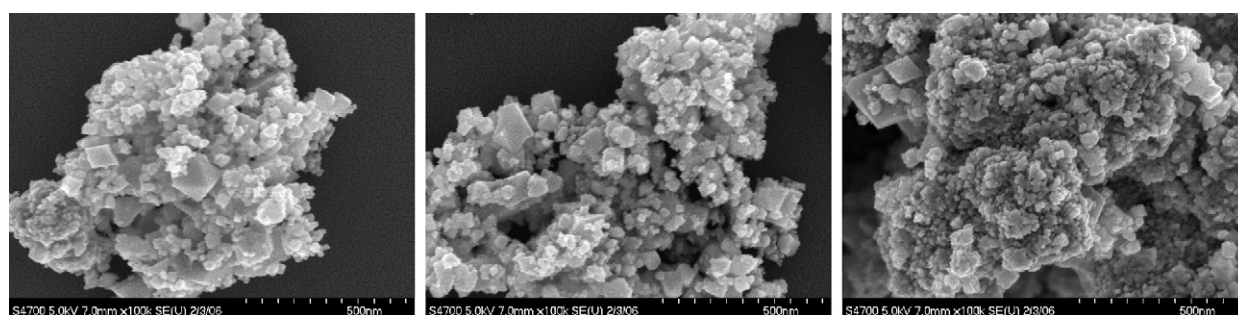


Fig. 10. High resolution SEM images of 40 wt.% Pt on ITO.

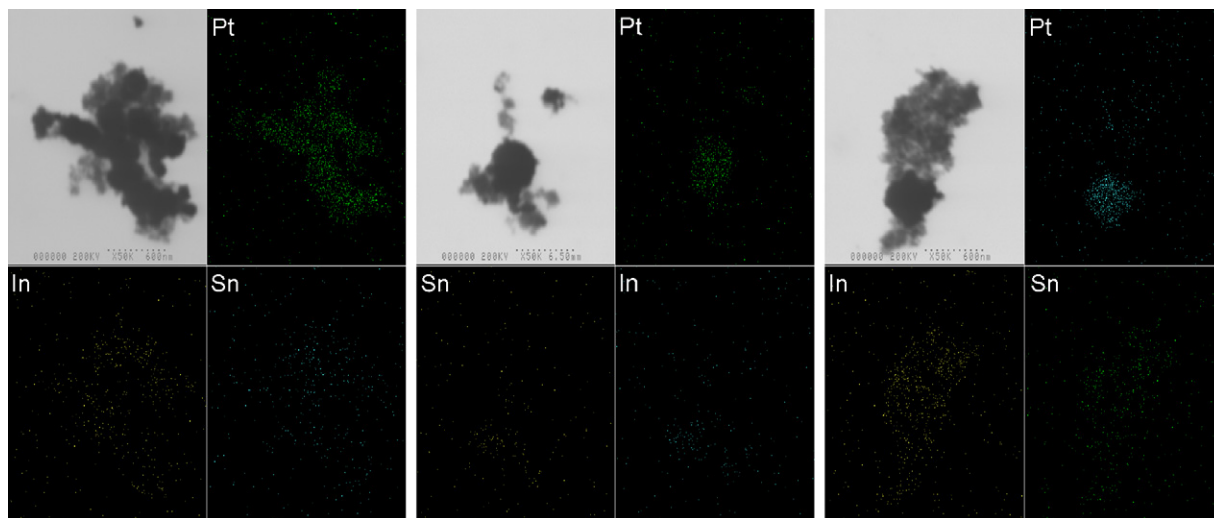


Fig. 11. TEM EDX of 40 wt.% Pt on ITO.

Fig. 11 shows three TEM images of 40% Pt on ITO. The EDX data indicate that Pt clusters are dispersed on small ITO particles. Further microstructural optimization can lead to further increases in overall electrochemical activity.

4. Conclusions

It has been demonstrated that indium tin oxide (ITO) may have potential for use as a catalyst support in PEMFCs. The

ITO support is more stable to oxidation than Vulcan XC-72R in Hispec 4000 or in Pt deposited on Vulcan XC-72R using the same process as for the ITO. The ITO supported catalyst had a lower electrochemically active surface area loss under accelerated voltage cycling, and lower mass loss in TGA experiments compared to the Pt/carbon catalysts studied. Therefore, ITO has potential as an oxidation-resistant candidate material for catalyst supports in a PEMFC. Further studies are required to optimize the particle size distribution and dispersion of the catalyst and

support particles, along with performance characterization in a working fuel cell cathode.

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