

**Corrosion of Transition Metals in  $Pt_{1-x}M_x$  ( $M = Fe, Ni, Mn$ ) Proton Exchange Membrane Fuel Cell (PEMFC) Electrocatalysts**

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In the past decade, platinum transition metal alloys such as PtNi, PtCr, PtCo, have been studied as oxygen reduction reaction (ORR) electrocatalysts for proton exchange membrane fuel cells (PEMFC) [1]. These alloys generally lead to a 20-40mV gain in the activation of ORR, where about 70% of the PEMFC losses occur [2]. Toda et.al. for example have shown volcano behavior in the catalytic activity of sputter deposited PtM ( $M=Ni, Co, Fe$ ) alloys [3].

The long term stability of these alloys and the corrosion of the transition metals under the fuel cell operating environments has not been discussed in the literature very widely. The corrosive environments of typical PEM fuel cells ( $pH \leq 1, T=80^\circ C$ ) could lead to leaching of transition metals like Ni, Fe which are not Pourbaix stable in the E-pH regions of PEMFC.

The aim of this study was to simulate leaching of transition metals from Pt alloys using heated acid and to compare the results with the alloy compositions after operation in PEMFC. A wide range of binary (Pt-M) alloys were prepared using a combinatorial magnetron sputtering method developed at Dalhousie University. The films were sputtered onto organic based nano-structured thin film (NSTF) substrates which consist of self-assembled whisker-like structures (500nm long, and 50nm in diameter). This technology has been developed at 3M Co. Development of NSTF, catalyst coating, and early PEMFC results are reported by M.K. Debe [4]. The films were characterized by X-ray diffraction (XRD) and electron microprobe before and after treatment in 0.3 and 1M acid ( $H_2SO_4$  and  $HClO_4$ ) at different temperatures ( $25^\circ C, 55^\circ C, 80^\circ C$ ). Detailed results for composition and structural changes of  $Pt_{1-x}M_x$  ( $M=Ni, Fe, 0 < x < 1$ ) alloys after acid treatments are reported elsewhere [5]. Fuel cell measurements were performed in  $H_2/O_2$  cell using Nafion (117) at  $80^\circ C$ .

The findings in all cases show very good agreement between the acid treated and FC tested samples. Here three sets of data for combinatorial libraries  $Pt_{1-x}Mn_x, Pt_{1-x}Fe_x$ , and  $Pt_{1-x}Ni_x$  are shown in Figure 1, respectively. Figure 1a,b,c show the Mn, Fe, and Ni contents after fuel cell testing and after acid treatment in 1M  $H_2SO_4$  ( $80^\circ C$ ) plotted versus the transition metal content of as-deposited  $Pt_{1-x}Mn_x, Pt_{1-x}Fe_x$ , and  $Pt_{1-x}Ni_x$  libraries. Figure 1 clearly shows that Mn, Fe, and Ni contents are reduced at all points of the library. After fuel cell testing, the transition metal content is no more than  $x = 0.25$  for any position in the library.

The impact of acid treatment on the crystallographic structure of the  $Pt_{1-x}Fe_x$  films, are shown in Figure 2. Inclusion of Fe (or Ni) decreases the lattice constant of the fcc structured alloy. For  $x < 0.5$ , no substantial changes in the lattice constant was observed after acid treatment; whereas for  $x > 0.5$ , the lattice constant increased after acid treatment indicating that Fe atoms have dissolved from the bulk of the grains.

**References**

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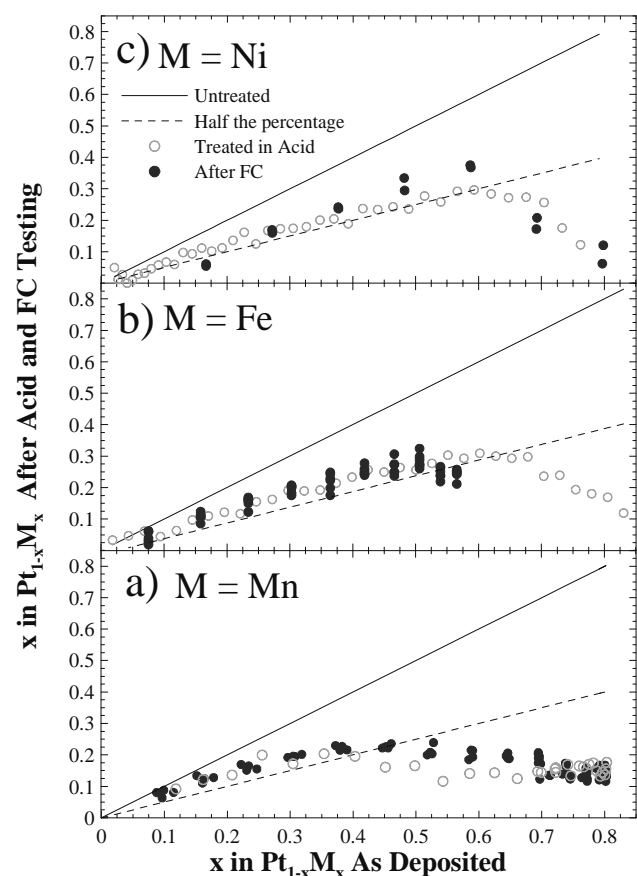
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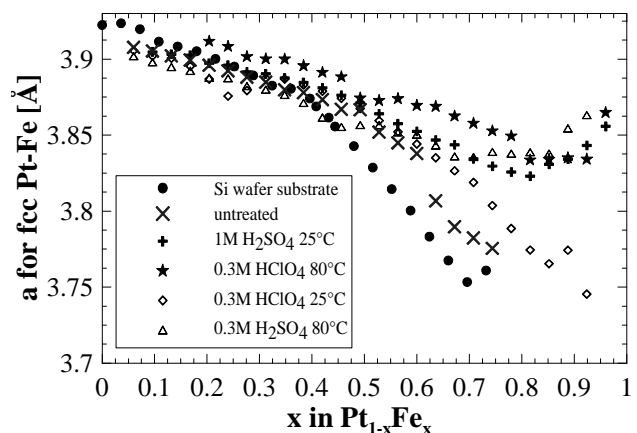
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**Figure 1.** Composition of the acid treated and fuel cell tested  $Pt_{1-x}M_x$  ( $M = Mn, Fe, Ni$ ) libraries.



**Figure 2.** Variation of lattice constants versus  $x_{before}$  in  $Pt_{1-x}Fe_x$  for acid treated  $Pt_{1-x}Fe_x$  libraries. Note that the lattice constants of the acid treated samples differ from the untreated sample for  $x_{before} > 0.5$  in  $Pt_{1-x}Fe_x$ .