

Limiting the amount of oxides in Pt-Mn alloy catalysts for ethanol oxidation

E. Bradley Easton, M. R. Zamanzad Ghavidel,
O'Rian Reid, Malika Ammam, Laura E. Prest

Faculty of Science (Chemistry)
University of Ontario Institute of Technology
2000 Simcoe St. N., Oshawa, ON
CANADA L1H 7K4

Improved ethanol oxidation catalysts are required to improve the commercial viability of direct alcohol fuel cells (DAFC) for power generation applications and also to lower the costs associated with breath alcohol detection devices. Current research efforts are focused on increasing the intrinsic activity of the catalysts and reducing the amount of Pt required to achieve acceptable performance. The most common approach to this problem is to synthesize alloys of Pt with other transition metals (TM). A wide array of binary Pt-TM alloys has been reported in the literature, including Ru, Sn, Mo, Rh or Pb. Since all of these alloying metals are oxophilic, often a significant amount of TM-oxide is produced along with a binary alloy. This often makes it difficult to attribute any improved performance sole to either the enhanced intrinsic activity of the pure alloy phase or a promotion effect of the metal oxide.

We have recently reported have reported Pt-Mn alloy catalysts with high catalytic activities towards ethanol oxidation [1]. A detailed study of alloy stoichiometry revealed that the highest intrinsic activity results with catalysts that have relatively low Pt-contents. XRD measurements indicated that alloy formation had occurred, however particle sizes were somewhat larger and an appreciable amount of manganese oxides were present in all catalysts.

In effort to improve the activity of this Pt-Mn system, synthetic parameters were modified with the goal of reducing particle size and also to control the amount of manganese oxide present. Figure 1 shows that by sparging the solution with N₂ during alloy particle formation/deposition yields catalysts with greater activity towards ethanol oxidation. Likewise, post-deposition heat treatment of the catalysts had a significant impact on catalytic activity, with a marked increase in activity when annealing was performed at 900 °C as shown in Figure 2.

Here we will present an overview of the impact of changing the synthetic parameters on the ethanol oxidation activity. Structural information (from TEM, XRD and XPS) will also be used to correlate the

ethanol oxidation activity with amount of surface oxide present.

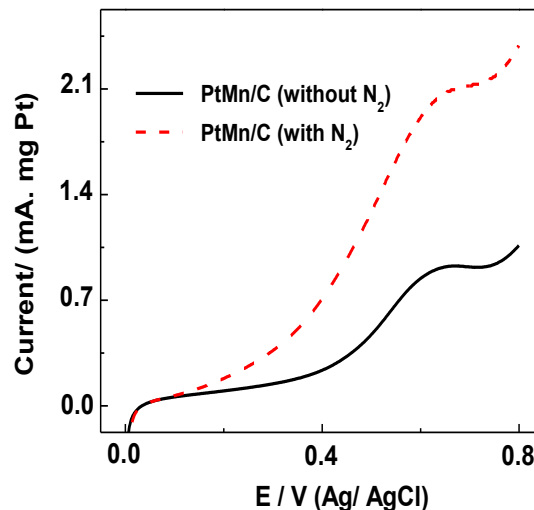


Figure 1. Linear sweep voltammograms obtained for Pt_{0.18}Mn_{0.81}/C synthesized without and with N₂-sparging during deposition. Measurements were made in 0.5 M H₂SO₄ containing 0.17 M ethanol.

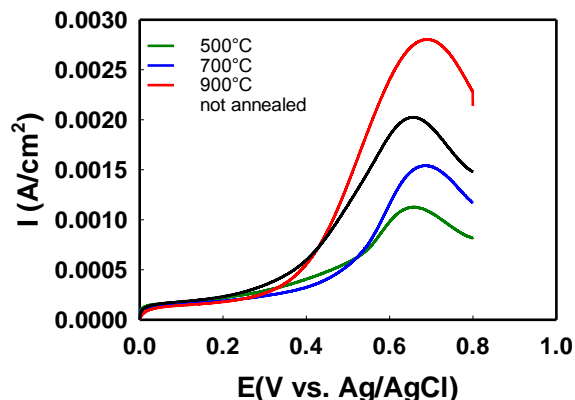


Figure 2. Linear sweep voltammograms obtained for Pt_{0.25}Mn_{0.75}/C catalysts that were annealed at different temperatures. Measurements were made in 0.5 M H₂SO₄ containing 0.17 M ethanol.

References

1. M. Ammam, L. E. Prest, A. D. Pauric, and E. B. Easton, *J. Electrochem. Soc.*, **159**, B195 (2012).