

Electrocatalyst Materials for PEM Fuel Cells Based on iron or vanadium substituted Heteropoly Acids

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The Heteropoly acids (HPA) a large and diverse class of inorganic materials that can act as redox catalysts when substituted by a transition metal, are proton conductors, and can be reduced to form electronically conducting materials. This makes the HPA ideal candidates for an electrode material in a PEM fuel cell in which the catalyst would ideally enable fast transfer of protons and electrons as well as be a selective catalyst on the nano-scale. Functionalized heteropoly acids, HPA, based on iron and vanadium have the potential to act as cost effective catalysts for fuel cell oxidations as well as facilitate both proton and electron conduction.

Two carbons have been investigated by Ambersorb-572 and XC-72 as provided in conventional GDEs. The loadings of HPA on the XC-72 carbon based GDEs are very low, typically 0.1 mg/cm². After conditioning the MEA current densities are typically on the order of 100 mA/cm² at 0.1 V using H₂/O₂, but the OCV of 0.75 V is somewhat low presumably due to the poor activation of the iron catalyst compared to platinum. When the MEA is turned over and the iron-substituted HPA is run as the anode an electrochemical wave is observed. After exposure to H₂ as the anode the catalyst improves to give close to 150 mA/cm² under the same conditions on the cathode, Figure 1. This activity appears to be stable. multiple polarization curves can be run after the reduction step. When O₂ is switched for N₂ on the cathode and successive polarization curves are run the limiting current density falls, initially rapidly and then more slowly, Figure 2. As there is no oxygen to regenerate the catalyst the activity is diminished with each successive sweep. The rapid fall of current density is due to the reversible depletion of the oxygen from the iron centers. The slow fall in activity at longer times/lower current densities is due to the irreversible depletion of skeletal tungsten bound oxygen. When the catalyst is depleted under N₂ only to the end of the rapid reversible current density loss we would expect it to recover all its activity on re-exposure to O₂. Interestingly the catalyst performs better and better on each successive cycle of experiments. From these results we speculate that electrochemical or chemical reduction of these iron substituted HPA results in the formation of iron/tungsten oxide nanoparticles that may be the true catalyst.

We have also investigated vanadium substituted HPA [1]. These materials exhibit very similar behavior to the iron-substituted HPA, but limiting current densities achieved on the cathode are only 24 mA cm⁻² at 80 °C. The temperature dependence of the catalytic activity improves dramatically with temperature leading us to believe that these may be very interesting catalysts for higher temperature PEM fuel cells. These vanadium substituted HPA materials are much more interesting

when used as a co-catalyst on the fuel cell anode, Figure 3. A 30% improvement in current density and power is seen with the vanadium HPA/Pt versus the Pt catalyst. Control experiments with and without Nafion® in the electrodes indicate that at least some of this activity is due to the proton conducting ability of the HPA. Additional controls with unsubstituted HPA and V₂O₅ indicate that the catalytic activity only originates from the vanadium substituted HPA and in addition the catalyst must contain more than two vanadium atoms.

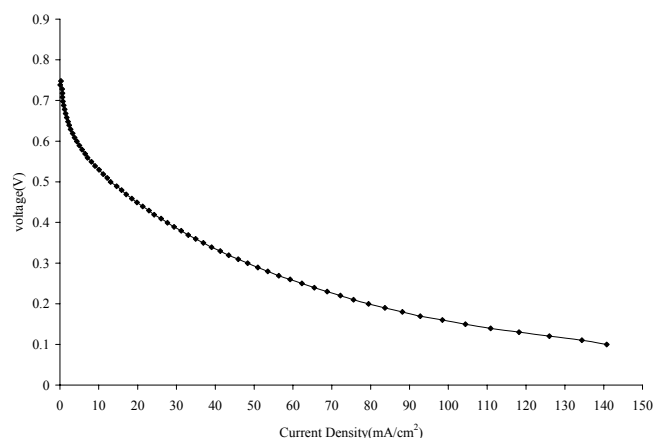


Figure 1. Polarization curve for an iron substituted HPA after reduction on the cathode and Pt on the anode on ELAT GDE at 80 °C, using H₂/O₂ humidified at 90 °C.

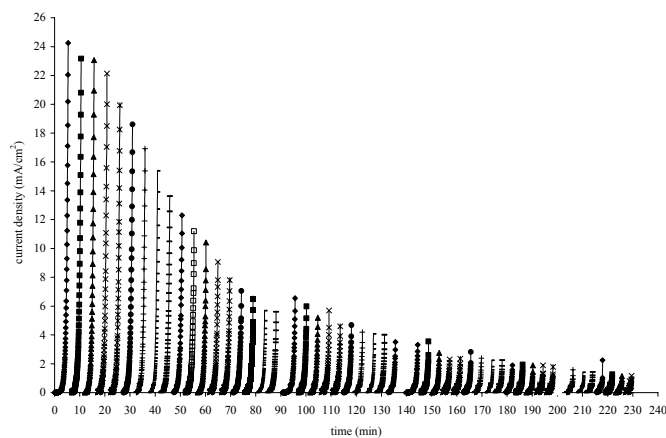


Figure 2. Successive polarization curves for an iron substituted HPA after O₂ exposure on the cathode and Pt on the anode on ELAT GDE at 80 °C, using H₂/N₂ humidified at 90 °C.

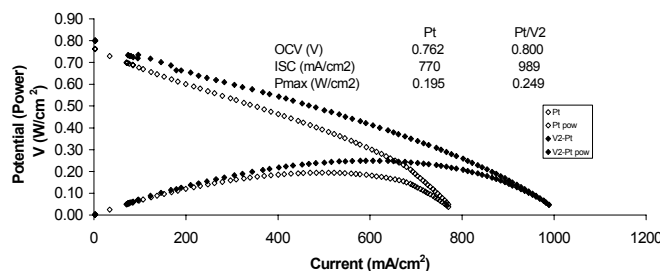


Figure 3. Polarization and power curves for Pt on ELAT electrodes as both anode and cathode catalysts and for a vanadium substituted HPA/Pt co-catalyst system as anode with a Pt cathode.

(1) Limoges, B. R.; Herring, A. M.; Turner, J. A. *Electrochimica Acta*, Submitted.