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Short communication

The use of the heteropoly acids, $H_5PMo_{10}V_2O_{40}$, $H_7[P_2W_{17}O_{61}(Fe^{III}\cdot OH_2)]$ or $H_{12}[(P_2W_{15}O_{56})_2Fe_4^{III}(H_2O)_2]$, in the anode catalyst layer of a proton exchange membrane fuel cell

Mei-Chen Kuo [a], Bradford R. Limoges [a], Ronald J. Stanis [a,b],
John A. Turner [b], Andrew M. Herring [a,*]

[a] *Department of Chemical Engineering, Colorado School of Mines, Golden, CO 80401, United States*
[b] *Hydrogen and Electricity Systems and Infrastructure Group, National Renewable Energy Laboratory, Golden, CO 80401, United States*

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Abstract

The use of heteropoly acids (HPAs) in PEM fuel cell anode catalyst layers was studied. To compare the doped electrodes with a control electrode in a meaningful way membrane electrode assemblies (MEAs) were prepared with two 1/2 anodes, one the undoped control and one the test electrode. This ensured that both the control and test electrode were subject to the same thermal and electrochemical history. After curve fitting the data using a least squares method the error was found to be 1% in E_0, 25% in the Tafel slope and 15% in the area specific resistance. The electrodes used were commercial electrodes of the Los Alamos type (ELATs). Doping a fuel cell anode with $H_5PMo_{10}V_2O_{40}$ resulted in a fourfold increase in the area specific resistance of the MEA, but the performance was not equivalent to that of an anode incorporating Nafion®. Doping $H_5PMo_{10}V_2O_{40}$ in Nafion® painted ELATs resulted in negligible improvements in the performance compared to ELATs incorporating only Nafion®. Much more impressive was the improvement in maximum power from doping the Nafion® painted ELAT with $H_7[P_2W_{17}O_{61}(Fe^{III}\cdot OH_2)]$ or $H_{12}[(P_2W_{15}O_{56})_2Fe_4^{III}(H_2O)_2]$. Eighty-five percent improvements in maximum power and 100% improvements in area specific resistance were observed from this HPA doped ELAT.

Keywords: PEM fuel cell; Gas diffusion electrode; Heteropoly acid; Interfacial resistance; Anode

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1. Introduction

The proton exchange membrane (PEM) fuel cell holds much promise as an efficient and versatile energy conversion device. However, in order for the PEM fuel cell to achieve widespread usage a number of key technical hurdles need to be overcome. These include the discovery of an efficient 4e⁻ oxygen reduction reaction (ORR) electrocatalyst, an anode catalyst that is at least as efficient as Pt for the hydrogen oxidation reaction (HOR) and is not easily poisoned by small molecules such as carbon monoxide, and a fuel cell membrane that can be operated at elevated temperatures without the need for external humidification for adequate proton conduction. For any or all of these approaches to succeed the catalyst/ionomer/electron conducting three-phase boundary must be engineered for maximum performance. The optimal design of the catalyst layer in the electrode is, therefore crucial, to the performance of the fuel cell.

In a conventional PEM fuel cell the perflourosulfonic acid (PFSA) PEM is attached to a platinum catalyzed anode on the hydrogen (fuel) side of the cell and a platinum catalyzed cathode on the oxygen (air) side of the cell. The platinum is supported on an electrically conductive high surface area carbon which is coated with the ionomer to fabricate a three-phase boundary, between proton conductor (ionomer), electron conductor and reactant gases. The standard ionomer in use in PEM fuel cells is a PFSA polymer such as Nafion® [1]. While much is known about the effect of PFSA ionomer loading and equivalent weight on the electrode performance in terms of ionic conductivity and porosity [2–4], very little is known about the use of other proton conducting materials in the PEM fuel cell catalyst

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[*] Corresponding author. Tel.: +1 303 384 2082; fax: +1 303 273 3730.
E-mail address: aherring@mines.edu (A.M. Herring).

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layer [5]. In fact most catalyst layers with new membranes contain Nafion® as the sole ionomer, although a patent proposing inorganic proton conducting materials has been granted [6]. The use of zirconium hydrogen phosphate in fuel cell electrodes has been shown to be beneficial to high temperature operation [7]. Such studies are important because they shed light on transport phenomena in the catalyst layer and point to new materials for enhanced performance. It will also be necessary to develop new ionomers for the catalyst layers in PEM fuel cells to utilize many of the promising novel proton conducting polymers [8] and composite materials [9] currently being developed. A thorough understanding of transport in the catalyst layer and proton transport from the catalyst layer to the PEM is essential to avoid large interfacial resistances in the fuel cell.

The heteropoly acids (HPAs) represent a class of inorganic proton conductors that also have interesting redox properties. The HPA and the zirconyly phosphates have been proposed as the proton conductor in PEM fuel cell catalyst layers [6,7]. Some HPAs have proton conductivities as high as 0.2 S cm^{-1} representing some of the highest known proton conductivities measured in the solid state [10,11]. When reduced, the HPAs also become capable of electron conduction giving rise to a mixed electronic/protonic conductor. Such a material could dramatically improve electronic and protonic conduction in the fuel cell anode. We have been studying a number of different HPA in the solid state and their impact on the performance of the fuel cell membrane electrode assembly (MEA) in the absence of platinum [12,13]. In this paper we now report on the use of HPAs in the anode layer of the PEM fuel cell MEA as a mixed protonic/electronic conducting additive in the PFSA platinum containing catalyst layer.

For this study we focused on a series of iron substituted HPA based on the Wells–Dawson structure [14]. The iron substituted HPA are interesting catalysts [15,16] and electro-catalysts [17,18]. Our original thought was that they would enhance the hydrogen oxidation reaction (HOR), but as the HOR on Pt is extremely rapid [19] it is much more likely that the observed effects are on proton and electron transport away from the catalyst and into the ionomer and current collector of the electrode layer. The Wells–Dawson HPA $[(X^{n+})_2M_{18}O_{62}]^{2n-16}$, where X^{n+} represents a central atom such as, P^{5+}, As^{5+}, or S^{6+}; surrounded by a cage of M addenda atoms, such as W^{6+} or Mo^{6+}, arranged in MO_6 octahedral units. The structure, of the α isomer, possesses two identical "half units" with the central atom surrounded by nine octahedral units XM_9O_{31} linked through oxygen atoms [20]. Non-saturated compounds such as, $XW_{11}O_{39}{}^{n-12}$ and $X_2W_{17}O_{61}{}^{2n-}$, called "lacunary" species are synthesized through the degradation of the Wells–Dawson anions in controlled basic media [20]. Iron may be substituted in the monolacunary HPA to yield $[P_2W_{17}O_{61}(Fe^{III}{\cdot}OH_2)]^{7-}$ but when substitution in the tri-lacunary HPA, the Wells–Dawson sandwich compound $[(P_2W_{15}O_{56})_2Fe_4{}^{III}(H_2O)_2]^{12-}$ is obtained, Fig. 1. Both of these HPA were isolated as the sodium salt and converted to the free acid by extraction from acid solution as the ether adduct. As the ether was not cooled the Wells–Dawson sandwich molecule had only two iron atoms [12]. We also report some preliminary data for Keggin HPA $H_5PMo_{10}V_2O_{40}$, not shown.

Small amounts of HPA are strongly adsorbed on to carbons. Such adsorbed HPA survive washing with water, necessary for removal of loosely bound HPA, and are robust enough that an MEA containing them can be brought to steady state and thoroughly studied for several days. In order to compare the HPA doped anode to the undoped anode control we prepared MEAs with both electrodes on the anode side. This ensured that each electrode was subjected to the same fabrication history and was conditioned to steady state under the same conditions. By use of a masked gasket we were able to independently measure each electrode to achieve a qualitative comparison.

2. Experimental

2.1. Materials

The HPAs, K_7 or $H_7[(P_2W_{17}O_{61})Fe^{III}(H_2O)]$ (KFe1, HFe1) and Na_{12} or $[(P_2W_{15}O_{56})_2Fe_4{}^{III}(H_2O)_2]$ and its disubstituted free acid analogue (NaFe4 and HFe2) were prepared and characterized as described previously [12,16]. α-$H_3P_2W_{18}O_{62}$ (Wells–Dawson) and $H_5PMo_{10}V_2O_{40}$ (HV2) was prepared by literature methods [21,22]. The number of waters associated with each HPA was determined by thermogravimetric analysis using a TGA/DTA 220 analyzer (Seiko Instruments Inc.) under He at 10 psi a from 25 to 300 °C at a rate of 5 °C min^{-1}.

The gas diffusion electrode (GDE) used was a single sided electrode Los Alamos type (ELAT) (E-Tek, De Nora, NA) loaded at 0.5 mg cm^{-2} Pt (20% Pt on Vulcan XC-72 carbon). GDEs were cleaned with boiling DI water and 3% H_2O_2 solution before use. The HPA doped GDEs were prepared as described previously for a doped GDL giving a typical loading of typically 0.04 mg cm^{-2} [12]. Nafion® 117 (Ion Power) was washed in successive boiling solutions of 3% H_2O_2, DI water, 0.5 M H_2SO_4, and DI water each for 1 h.

2.2. Preparation of split anode MEA

MEAs were prepared in the configuration shown in Fig. 2. The MEA was fabricated with a HPA doped Pt GDE (about 2.2 cm^2), and a Pt control GDE (about 2.2 cm^2), separated by a small gap on the anode and a larger Pt GDE (5 cm^2) on the cathode. The electrodes were hand painted with Nafion® solution (approx. loading: 1.8 mg cm^{-2}) and allowed to dry in the air. The electrodes were then pressed on to a Nafion® 117 membrane with a digital combo multi-purpose press (GEO Knight & Co. Inc.) at 115 °C and 80 psi for 90 s.

2.3. Measurements

Fuel cell measurements were made in 5 cm^2 active area hardware (fuel cell technologies) at 80 °C using saturated H_2 and O_2 (99.999%, general air) at 100% RH, humidifier (Lyntech Industries, Inc., FCTS BH) 90 °C dew-point. The gasses were metered at a flow rate 0.1 l min^{-1} of H_2 and O_2 with 30 psi backpressure (Lynntech Industry, Inc., FCTS GMET/H). The fuel cells were either tested against an electronic load (Lynntech Industries, Inc.,