

Electrocatalyst materials for fuel cells based on the polyoxometalates $[\text{PMo}_{(12-n)}\text{V}_n\text{O}_{40}]^{(3+n)-}$ ($n = 0-3$)

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Abstract

We report on the use of the polyoxometalate acids of the series $[\text{PMo}_{(12-n)}\text{V}_n\text{O}_{40}]^{(3+n)-}$ ($n = 0-3$) as electrocatalysts in both the anode and the cathode of polymer-electrolyte membrane (PEM) fuel cells. The heteropolyacids were incorporated as catalysts in a commercial gas diffusion electrode based on Vulcan XC-72 carbon which strongly adsorbed a low loading of the catalyst, ca. 0.1 mg/cm². The moderate activity observed was independent of the number of vanadium atoms in the polyoxometalate. In the anode the electrochemistry is dominated by the $\text{V}^{3+/4+}$ couple. With a platinum reference wire in contact with the anode, polarization curves are obtained with V_{OC} of 650 mV and current densities of 10 mA cm⁻² at 100 mV at 80 °C. These catalysts showed an order of magnitude more activity on the cathode after moderate heat treatment than on the anode, $V_{\text{OC}} = 750$ mV, current densities of 140 mA cm⁻² at 100 mV. The temperature dependence of the catalysts was also investigated and showed increasing current densities could be achieved on the anode up to 139 °C and the cathode to 100 °C showing the potential for these materials to work at elevated temperatures.

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1. Introduction

One of the barriers to the commercialization of proton exchange membrane (PEM) fuel cells fed with hydrogen as the fuel is the need for high loadings of expensive precious metal catalysts on both sides of the membrane, especially on the cathode where the oxygen reduction reaction (ORR) is sluggish [1,2]. Whilst acceptable loadings of platinum and platinum alloy catalysts have been achieved on the PEM fuel cell anode these electrodes can only be used with relatively pure hydrogen; carbon monoxide poisoning of the electrode remains a problem for hydrogen produced by the reforming of hydrocarbon fuels [3]. The discovery of a catalyst that performs as well as the platinum based catalysts at low temperatures, <100 °C, will be extremely challenging. There is an

ongoing research effort to operate PEM cells at elevated temperatures, >100 °C [2]. At these higher temperatures it may be possible to substitute the platinum catalysts with other less expensive catalysts that perform adequately for commercial PEM fuel cell operation. Much research has been performed in the use tungsten carbides as anode catalysts [4] and pyrolyzed iron porphyrins as cathode catalysts [5] as possible non-platinum fuel cell electrode materials.

Polyoxometalates, a large class of inorganic transition metal oxygen cluster compounds including the heteropolyacids (HPAs), have attracted increasing interest in the past couple of decades for their catalytic applications [6,7]. HPAs with the Keggin structure, and in particular the compounds $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$, have received particular attention due to their acidic and redox properties, stability at elevated temperatures, commercial availability and relative ease of synthesis [6,7]. HPAs are known proton conductors, which may be exploited in the design of the membrane

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electrode assembly (MEA). Depending on their chemical environment not all HPA lose all their bound water molecules below 100 °C, allowing the real possibility of proton conduction at elevated temperatures. These materials have even been investigated as possible electrocatalysts for fuel cell applications with limited success, [8,9] and have been shown to increase the tolerance of a platinum containing anode to deactivation by carbon monoxide [10]. There are many HPAs that are easily synthesized that have not been investigated as PEM fuel cell electrocatalysts. In surveying various HPAs for candidates as anode electrocatalysts, and as vanadium oxides have been demonstrated in partial oxidations [11,12] and some work has been done reduction of O₂ by reduced H₃PMo₁₀V₂O₄₀ [36], we alighted upon the series of compounds [PMo_(12-n)V_nO₄₀]⁽³⁺ⁿ⁾⁻ (n = 0–3) as likely candidates. In addition Mo HPA are more susceptible to reduction making them more likely to act as mixed electronic/protonic conductors facilitating the fuel cell three phase boundary. These vanadium substituted polyoxometalates have been used as selective oxidation catalysts for a variety of organic reactions [13] from ambient [14] up to temperatures of 300 °C [15]. Of particular interest to us, is their ability to oxidize molecular hydrogen and methanol [16]. The electrochemistry of vanadium substituted HPAs in acidic solution has been extensively studied [17–20]. HPAs are easily immobilized from aqueous solution by use of the appropriate carbon [21]. There are relatively few reports of non-metallic catalysts tested as fuel cell catalysts in an actual PEM fuel cell, i.e. where the catalyst is in contact with a solid polymer electrolyte [5,22]. As the vanadium substituted catalysts could potentially act as a solid state proton conducting catalyst, with the added possibility of electronic conduction on the fuel cell anode, we decided that it would be very informative to actually evaluate these catalysts in the MEA of a PEM fuel cell and this is the subject of this work.

2. Experimental

2.1. Materials

The acids of the [PMo_(12-n)V_nO₄₀]⁽³⁺ⁿ⁾⁻ (n = 1–3) series were prepared by literature methods [23]. H₃PMo₁₂O₄₀ was supplied by Mallinckrodt and was used as is.

Cloth gas diffusion electrodes (GDEs) and gas diffusion layers (GDLs) were supplied by E-Tek (De Nora, NA). The GDE was a single sided ELAT loaded at 0.35 mg/cm² Pt (20% Pt on Vulcan XC-72 carbon). The GDL was the same structure with an uncatalyzed carbon layer, A-10 ELAT/Development GDL/type V2.02 very thin. In some experiments a very thick GDL of similar construction was employed to increase the area loading of HPA, A-10 ELAT/Development GDL/V2.33, in which case the platinumized GDE used was of the same structure with a Pt loading of 0.5 mg/cm². A 5% Nafion[®] solution was supplied by Electro-Chem. Nafion[®] 117 membrane was supplied by Ion

Power. The Nafion[®] 117 membrane was pre-treated by boiling in 3% H₂O₂ for 1 h, followed by boiling in DI water for 1 h, followed by boiling in 1 N H₂SO₄ for 1 h, followed by 1 h in boiling DI water. It was then stored in DI water in the dark prior to use [24].

2.2. Catalyst loading

Unless otherwise noted, the catalyst was added to the GDL in the following manner. Approximately 0.5 g of the appropriate catalyst was dissolved in 15–20 mL H₂O in an ehrlenmeyer flask fitted with a condensing cap to prevent evaporation. The solution was stirred with a magnetic stir bar at low reflux. A 5 cm² piece of GDL was floated on the surface of the solution [25]. The solution was stirred for 24 h, the GDL was removed, rinsed with DI water and dried in an oven at 80 °C for 24 h. HPA loading was typically 0.1–0.2 mg/cm², as measured on a standard four place analytical balance on the very thin GDL and 0.1 mg/cm² on the thick GDL [26].

Solution cyclic voltammetry was performed on the PAR VersaStat II. A single compartment cell was used with a Pt working electrode, Pt wire counter electrode and a saturated calomel electrode as the reference. The electrolyte was 1 M HClO₄. The scan rate was 50 mV/s.

2.3. MEA fabrication

The MEA was composed of one GDE fabricated as above and one platinum catalyzed GDE with a loading of 0.35 mg/cm² of 20% Pt on Vulcan XC-72 carbon (E-Tek). Both electrodes were hand painted with Nafion[®] solution (approximately loading: 0.6 mg/cm²) and allowed to dry. The electrodes were pressed into Nafion[®] 117 with a Carver hydraulic press with heated platens at 130 °C and 75–100 psi for 90 s. The membrane of the MEA using the very thin GDE was not “conditioned”, as proton conduction across the membrane was not considered the limiting factor in the performance of our MEAs and no difference in performance was observed. The MEA with the very thick GDE were conditioned until steady state performance was achieved.

2.4. Equipment

The two test stands described below were used alternately to collect data on various (and occasionally the same) MEAs. The choice of stands was made purely on the sake of convenience and the two stands produced equivalent results.

The first stand is located at NREL and consists of a Globetech Compucell GT fuel cell test stand. This model has bubble humidifiers and custom made heated gas transfer lines. The backpressure is manually regulated. For the MEAs with the very thin GDE which only generated small currents, data was collected using a Princeton Applied Research VersaStat II potentiostat. For the MEA with the very thick GDE a Scribner load box was employed. The polarization curve was

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