



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Rotating disk electrode study of Pt/Cs₃HPMo₁₁VO₄₀ composite catalysts for performing and durable PEM fuel cells

Marco Renzi ^a, Pasqualina Mignini ^a, Gabriele Giuli ^b, Roberto Marassi ^a,
Francesco Nobili ^{a,*}

^a School of Science and Technology – Chemistry Division, University of Camerino, Via S. Agostino, 1, 62032 Camerino, MC, Italy

^b School of Science and Technology – Geology Division, University of Camerino, Via S. Agostino, 1, 62032 Camerino, MC, Italy

ARTICLE INFO

Article history:

Received 18 February 2016

Received in revised form

1 April 2016

Accepted 28 April 2016

Available online 24 May 2016

Keywords:

HOR

ORR

Polyoxometalates

Rotating disk electrode

PEM fuel cells

ABSTRACT

A polyoxometalates (POM) of Kegging-type structure, Cs₃HPMo₁₁VO₄₀ has been tested as mesoporous matrix to increase Pt electrocatalytic activity, by the enhancement of particles dispersion and active area. Physicochemical characterization has been carried out to clarify the structural properties of the matrix. SEM micrograph demonstrated a big change of the morphological features identifying POMs crystals with diameter less than 500 nm. The composite catalyst has been prepared by mixing the polyoxometalates with Pt/Vulcan XC72-R catalyst. By RRDE studies, an improvement in catalytic activity has been observed, both for HOR and ORR, for the layer modified with polyoxometalate matrix. Carbon monoxide adsorption/desorption processes have been also studied in order to evaluate any possible effect towards CO poisoning. Finally, the behavior of a fuel cell, prepared with a POM-modified cathode, was evaluated at 100% relative humidity, revealing that a lower Pt loading can be applied in presence of POM co-catalyst, yielding uncompromised and durable performance.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Proton exchange membrane fuel cells (PEMFC) are one of the most appealing technologies as clean and efficient energy conversion device applied to mobile and stationary devices [1–3]. Unfortunately the current high costs, mainly related to the use of noble metals as catalysts and of per-fluorosulphonated membranes [2], still remain a big limitation for the mainstream market uptake by this technology. The

composition of the membrane electrode assembly (MEA) determines the overall performance and costs of the fuel cell. The catalytic sites where the hydrogen oxidation (HOR) and oxygen reduction reactions (ORR) occur are mainly based on noble-metal catalysts dispersed as fine particles on high surface area carbon support [4]. The use of noble metals, and mainly of Pt, is necessary because the ORR needs a very efficient catalysis for the cleavage of O=O bond [5]. Other metals also show high catalytic activity, but in acidic electrolytes

* Corresponding author. Tel.: +39 0737 402210; fax: +39 0737 402296.

E-mail address: francesco.nobili@unicam.it (F. Nobili).

<http://dx.doi.org/10.1016/j.ijhydene.2016.04.194>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

noble metals retain the greatest stability towards corrosion or passivation [6]. However, Pt is an expensive metal, which limits the widespread diffusion of the technology. As a consequence, much effort has been undertaken to find cheaper electrocatalysts with comparable activity. Materials cost of PEMFCs could be reduced by replacing Pt at the cathode with non-noble-metal catalysts (NNMCs) [7]. Co- and Fe-macrocycles were found to be good catalysts in acid medium, and Fe/N/C or Co/N/C electrocatalysts in PEM fuel cells have been widely studied due to their promising performance [8]. In particular, it has been demonstrated that high-surface-area Co/C catalyst can rival Pt/C under specific operating conditions [9]. Unfortunately, most of the catalysts above mentioned and reported in the literature, are not stable in operating fuel cells, even for relatively short times (currently, the focus of many research groups is to understand the cause(s) of instability of Fe/N/C or Co/N/C catalysts) [10].

As an alternative route for catalytic layer cost reduction, the development of a support, where the metal amount can be reduced, has been proposed because of better dispersion and limited aggregation upon working conditions [11]. This is seen as one of the most challenging, but at the same time promising, tasks to be accomplished in order to develop cheap, affordable and durable fuel cell devices [12].

In this context, heteropolyacids have been reported in some recent papers both as possible substrates alternative to carbon, and as efficient co-catalysts for redox processes, thanks to their high acidity and porosity. These features provide a high proton concentration on catalytic sites, and avoid the aggregation of catalytic particles during the fuel cell operation.

Heteropolyacids of Kegging type are very relevant because they can adsorb Pt nanoparticles; unfortunately due to their high water solubility they are prone to lose rapidly catalytic activity [13]. Therefore, the effort to enhance stability has been undertaken by preparing insoluble heteropolyacids salts, by partly exchanging protons with larger cations (Cs^+ in the present paper). Polyoxometalates (POMs) have been used since before 1900 in catalysis, medicine, biology, material science and topology [14]. The first POMs successfully applied to the catalysis of HOR and ORR were the ammonium phosphomolybdate and the similar phosphotungstate [15], which demonstrated enhanced catalytic performance, with respect to commercial Pt and Pt alloys, toward oxidation of Hydrogen and reduction of Oxygen [13,16,17]. In addition, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ has been demonstrated to be an excellent mesoporous support for Pt nanoparticles in the preparation of PEM electrodes with low Pt content [18]. The ability to trap Pt inside the porous matrix, preventing aggregation, resulted in durable electrochemical performance, a feature very important in the field of transportation, stationary and portable power [19–21]. The hydrogen oxidation reaction (HOR) is a fast reaction, and consequently only marginal improvement of kinetics may be expected [22]. On the contrary, for the oxygen reduction reaction (ORR) more relevant enhancements may be foreseen by enhancing Pt active surface, as well as proton and electron availability.

In this context, the present paper deals with the synthesis and the physico-chemical characterization of mixed Mo–V polyoxometalates and with their use as co-catalysts

supporting active Pt nanoparticles, evaluating their impact on the kinetics of HOR and ORR processes by advanced electrochemical techniques.

Experimental

Catalyst preparation

Preparation of POM insoluble salt [23] was carried out by the following steps. An aqueous solution of Cesium Carbonate (Cs_2CO_3 , Sigma–Aldrich $\geq 99.00\%$) was added drop-wise to Phosphovanadomolibdic acid ($\text{H}_4\text{PMo}_{11}\text{VO}_{40}\cdot 8\text{H}_2\text{O}$, hereafter labeled as PVM1-11, Nippon Inorganic Colour & Chemical CO., LTD.) solution under vigorous stirring in a water bath at 30°C . The fine suspension was held at 30°C overnight and subsequently evaporated to dryness at 50°C . A salt of stoichiometry $\text{Cs}_3\text{H}_1\text{PMo}_{11}\text{VO}_{40}$, hereafter labeled as POM3-1-1, was obtained (this stoichiometry is known [24] to exhibit the highest mesoporosity).

RRDE electrode preparation

A catalytic ink for cyclic voltammetry (CV) tests was prepared by mixing the synthesized salt POM3-1-11 with 20% Pt on Vulcan XC-72R (Pt/C, E-Tek Division) in $985\ \mu\text{l}$ of isopropanol. Immediately after, $15\ \mu\text{l}$ of Nafion[®] solution 5 wt% (Ion-Power, Inc.) were added and the slurry was put under vigorous stirring overnight. A mass ratio POM3-1-11:Pt:Nafion 1:1:1 has been used (labeled as Pt/POM ink). As a term of reference, an ink with bare Pt on Vulcan, with a mass ratio Pt:Nafion 1:1, has been prepared (labeled as Pt/C ink).

The catalytic ink was deposited as quickly as possible on the surface of a glassy carbon (GC) electrode through a Hamilton 701n $10\ \mu\text{l}$ -syringe and left to dry for 30 min in air, in order to obtain a Pt loading on the electrode of about $15\ \mu\text{g}/\text{cm}^2$. Electrolyte solutions have been prepared using Sulphuric acid (99.999%, H_2SO_4 , Sigma–Aldrich) or Perchloric acid 70% (redistilled, 99.999% metal basis, HClO_4 , Sigma–Aldrich). All the electrolyte solutions were initially degassed with N_2 for at least 30 min before every experiment. All the catalytic layers have been activated by 30 min of cyclic voltammetry at $50\ \text{mV}/\text{s}$ under nitrogen atmosphere (until stable voltammograms were obtained), in order to obtain a clean Pt surface.

Fuel cell MEA preparation

The ink was prepared by following the same procedure reported in Section RRDE Electrode preparation, but with a mass ratio Pt/C:POM:pure Nafion of 2:1:1. Pt loading was $0.2\ \text{mg}/\text{cm}^2$. The slurry was brushed on the gas diffusion layer (GDL) as uniformly as possible to obtain a homogenous thickness throughout all the electrode surface. The MEA has been prepared by sandwiching a Nafion 112 membrane of $60\ \mu\text{m}$ thickness (Ion-Power, Inc.), pre-treated with H_2O_2 and H_2SO_4 to remove organic and inorganic impurities [25,26], between anode and cathode at $P = 50\ \text{bar}$ and $T = 120^\circ\text{C}$ for 3 min. All the chemicals were used as obtained without further purification. Solutions were prepared using Millipore Milli-Q water of resistivity $\approx 17\ \text{M}\Omega\ \text{cm}$.

Download English Version:

<https://daneshyari.com/en/article/1269550>

Download Persian Version:

<https://daneshyari.com/article/1269550>

[Daneshyari.com](https://daneshyari.com)