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Rotating disk electrode study of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as mesoporous support for Pt nanoparticles for PEM fuel cells electrodes

S. Dsoke[a,1], A. Kolary-Zurowska[a,b], A. Zurowski[a,b], P. Mignini[a],
P.J. Kulesza[b,**], R. Marassi[a,*]

[a] Department of Chemistry, University of Camerino, S. Agostino 1, I-62032 Camerino, Italy
[b] Department of Chemistry, University of Warsaw, Pasteura 1, PL-02-093 Warsaw, Poland

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ABSTRACT

The catalytic activity of Pt nanoparticles supported by zeolite-type mesoporous $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ solid super-acid towards oxygen reduction has been explored. Pt(IV) impregnated $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared by titration of an aqueous solution of phosphotungstic acid and a known quantity of H_2PtCl_6 with a solution of cesium carbonate. The H_2PtCl_6 impregnated insoluble salt was subsequently chemically or electrochemically reduced to form supported Pt nanoparticles.

HRTEM micrographs show that the reduced composites Pt–$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Pt–$Cs_{2.5}PW_{12}$) contains Pt nanoparticles of average dimensions 2–5 nm, embedded into the porous structure of the insoluble salt. RDE and RRDE studies and fuel cell polarization data performed using thin layer composite films of Pt–$Cs_{2.5}PW_{12}$ chemically or electrochemically reduced show that the catalyst is very stable and rather efficient for oxygen reduction (ORR). The oxygen reduction wave is shifted by 60–70 mV towards more positive potentials with respect to the one obtained using electrodes prepared with a standard catalyst such as E-Tek 20% Pt–Vulcan. Analysis of the voltammetric curves demonstrates that the electrocatalytic activity of the composite electrodes is higher than that of the standard catalyst. This indicates that the solid state super-acid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ acts as co-catalyst by providing a proton rich environment in the vicinity of the Pt nanoparticles that enhances their catalytic activity towards oxygen reduction.

1. Introduction

Durability and cost are the most important issues that must be solved for a successful commercialization of proton exchange membrane fuel cells (PEMFC). Carbon supported Pt nanoparticles are by far the most used catalyst for oxygen reduction (ORR) and hydrogen oxidation (HOR) in PEMFC. Different problems, related to degradation of the Nafion membrane and carbon catalyst support, together with loss of catalytic activity of the Pt electro-catalyst, are currently important topics of basic and applied research worldwide [1,2]. Because of the high acidity, positive electrochemical potential and of the presence of water and oxygen in high concentration, the catalyst at the cathode side is particularly prone to degradation. Carbon oxidation at high potentials, enhanced by the presence of Pt, decreases the contact between the nanoparticles and the support that becomes increasingly hydrophobic causing a deterioration of the mass transport properties of the gas diffusion electrode (GDE). Loss of contact between the Pt nanoparticles and the carbon support also increases the mobility of the particles that might aggregate thus decreasing the electrochemical active surface area. Pt dissolution, and oxide formation at high potentials followed by re-deposition also contribute to the increase of the particle size [1–7].

In the attempt to solve or minimize these problems, current research follows different lines. Apart from optimizing the operating conditions by avoiding high potentials and humidity levels, one approach is the search of alternative matrices for supporting Pt nanoparticles. Several papers deal, for instance, with the use of TiO_2 [8–15] as support for Pt nanoparticles. Composite electrodes are formed by adding carbon to the Pt/TiO_2 in order to create a percolating path for electronic conductivity. As the Pt nanoparticles are supported on TiO_2, the direct contact of Pt with carbon is minimized and the carbon degradation is reduced. Interesting is also the use of electrodes in which Pt is supported on tungsten oxides [11,16–18]. These types of electrodes have been demonstrated to be able to promote oxygen reduction via hydrogen spillover. The highly conductive tungsten oxide bronzes are also effective in reducing formation of hydrogen peroxide.

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[*] Corresponding author. Tel.: +39 737 402214.
[**] Co-corresponding author. Tel.: +48 22822020211.
E-mail addresses: roberto.marassi@unicam.it (R. Marassi), pkulesza@chem.uw.edu.pl (P.J. Kulesza).
[1] Present address: ZSW-Zentrum für Sonnenenergie und Wasserstoff-Forschung, Helmholtzstraße, D-89081 Ulm, Germany.

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Heteropolyacids in fuel cell research have been the subject of several papers especially because of their ability to strongly adsorb on metal or carbon electrodes and of their high acidic character. Several research groups have explored the ability of different types of heteropolyacids to modify unsupported or carbon supported Pt nanoparticles for oxygen reduction [19–24], methanol oxidation [25–32] or as additive in membranes [33–42].

In recent papers we have been concerned with the optimization of Pt-based electrocatalyst for oxygen reduction (ORR) by modifying the surface of Pt nanoparticles with adsorbed Keggin type H_2PtCl_6 based on Si or P heteroatoms and addenda atoms such as W or Mo [19–23]. Adsorption of heteropolyanions (especially $H_3PW_{12}O_{40}$) on Pt causes a shift of the voltammetric peaks relative to formation of Pt-oxo (PtOH or PtO) species towards more positive potential. Because of a larger potential window over which platinum is not covered with platinum oxide, adsorption and activation of oxygen molecules during electrocatalysis is facilitated. Due to the interaction between heteropolianions and Pt surface by mainly corner oxygen, only a few percent of interfacial reactive platinum atoms are blocked to the access of oxygen molecules [23].

In spite of the fact that the heteropolyacids are strongly adsorbed, long-term operation of this type of electrodes may cause desorption leading to loss of the catalytic activity. One possible alternative to improve long term stability of the electrodes is the use of water insoluble heteropolyacid salts that may be easily prepared by partially exchanging protons of the parent acid with the large cations such as Cs^+, K^+, $NH_4{}^+$. The insoluble cesium salts of phosphotungstic $H_3PW_{12}O_{40}$ acid are of particular interest [43–49]. These salts are efficient solid acid catalyst for a variety of organic reaction. Partial substitution of protons in $H_3PW_{12}O_{40}$ by Cs^+ ions leads to formation of crystalline aggregates with peculiar changes of the surface area and surface acidity. The surface of $Cs_xH_{3-x}PW_{12}O_{40}$ is practically the same of that of the parent acid (about $5\,m^2\,g^{-1}$) up to $x=2$ and then rapidly increases with increasing x to reach values in excess of $100\,m^2\,g^{-1}$ ($135\,m^2\,g^{-1}$ for $Cs_{2.5}H_{0.5}PW_{12}O_{40}$) due to formation of a microporous/mesoporous structure [50] with interparticles voids. The surface acidity parallels the trend of the surface area: it increases with a bell-shaped behavior starting from $x=2$, reaches a maximum at $x=2.5$ and then decreases to zero for $x=3$. The high acidity together with the possibility to tailor the dimension of the pores has been largely exploited in organic chemistry for the development of shape selective catalysts. The surface protons are, in addition, highly mobile. This property, directly correlated with the hydration degree of the compound, has been explored in fuel cell research using pellets of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as electrolyte [51] or in the development of self-humidifying Nafion or sulfonated poly(ether ether ketone) (SPEEK) based membranes [37,38,41,42].

The catalytic activity of solid acids cesium salts towards a variety of organic reactions has also been improved by doping the water insoluble salts with precious metals such as Pt or Pd to obtain a bi-functional shape selective catalyst [49,52–55]. Pt doped $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Pt–$Cs_{2.5}PW_{12}$) has also been used as additive in SPEEK based membranes to reduce the hydrogen crossover in PEMFC. The Pt nanoparticles catalyze the hydrogen oxidation without affecting the insulating property of the membrane as the salt is an electronic insulator [41]. If one exclude the use of Pt–$Cs_{2.5}PW_{12}$ in membranes [41], to the best of our knowledge, the electrochemical characterization for oxygen reduction (ORR) (or hydrogen oxidation (HOR)) of composites electrodes using Pt nanoparticles supported on insoluble mesoporous salts of heteropolyacids under the conditions found in fuel cells has gone unreported. The basic idea behind this is similar to that exploited for TiO_2 or WO_3 with two possible additional advantages. The nanoparticles can be trapped inside the porous matrix mitigating/preventing particle aggregation. The electrodes may take advantage of the strong surface acidity of the compound and of the high proton mobility that may improve the kinetic of oxygen reduction that requires protons in addition to electrons. At the same time the high porosity of the salts should not affect the transport properties of the catalytic layer. As was the case of Pt nanoparticles supported on TiO_2, because of the insulating characteristic of the insoluble salts, the composite must necessarily contain a carbon additive to create a percolating electron-conducting network in the electrode. Recent patents applications deal with the description of the use of several Pt doped heteropolyacid salts in fuel cell research [56,57]. Activation of carbon-supported Pt nanoparticles by mixing with Cs salts of polyoxometallates of molybdenum and tungsten towards oxidation of methanol and ethanol has also been recently reported [58]. The same approach has also been used to enhance the ORR catalytic ac activity of carbon supported Pt–Co alloys [59]. A short report in which Pt doped $Cs_{2.5}PW_{12}$ was electrochemically prepared using a sacrificial Pt anode and used as ORR catalyst has also been published [60]. This paper deals with a study of chemically prepared Pt–$Cs_{2.5}PW_{12}$ composite electrodes with special concern to ORR using mainly RDE and RRDE voltammetry. Preliminary fuel cell data are also presented.

2. Experimental

2.1. Materials

All the chemicals were of analytical grade purity and were used without further purification. Phosphotungstic, perchloric and sulfuric acids, as well as chloroplanic acid, were obtained from Sigma Aldrich. Solutions were prepared using doubly distilled and subsequently de-ionized (Millipore Milli-Q) water. The carbon supported platinum catalyst (20% Pt/Vulcan XC-72), Vulcan-XC-72 and GDE (gas diffusion electrode) Pt loading $0.5\,mg\,cm^{-2}$ were from E-Tek. Nafion (5% alcoholic solution) and Nafion 212 membrane were obtained from Ion-Power, Inc.

2.2. Catalyst preparation

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($Cs_{2.5}PW_{12}$) was prepared [45] using the following steps. An aqueous solution of Cs_2CO_3 was added drop-wise to an $H_3PW_{12}O_{40}$ solution under vigorous stirring. The fine suspension was held at room temperature overnight and subsequently evaporated to dryness at 323 K. The ratio polyacid–cesium carbonate was regulated in such a way that the final stoichiometry corresponded to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. ICP-MS measurements on the dried solid gave a ratio Cs to W equal to 2.5 ± 0.05.

Pt(IV) containing solids were prepared in the same way starting from the heteropolyacid solution containing H_2PtCl_6 in different quantities depending on the desired final Pt metal content. The absence of any washing step assures that all the platinum present in the initial solution remains in the dried powder either adsorbed or trapped inside the pores of the insoluble salt. The product color is pale yellow reflecting the color of chloroplatinic acid. The prepared sample will be indicated in the following as Pt(x%)–$Cs_{2.5}PW_{12}$ with x indicating the final metal Pt loading in the salt.

Two different routes were followed to reduce the Pt(IV) to Pt: the dried solid was reduced using a 5% H_2/Argon stream at 300 °C or the Pt(IV) impregnated salt was used as such to prepare inks that were activated in situ by electrochemical means. Details on the latter procedure will be given in Section 3.

Electrodes for fuel cell experiment were prepared by brushing inks, having the same composition used for the film electrodes, containing either reduced or unreduced composites on Teflon treated Toray Carbon Paper (EC-TP1-060T) in the desired amounts. The MEA, were prepared by hot pressing (50 bar) the electrodes