J. of Supercritical Fluids 97 (2015) 154–164

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Electrochemical performance of fuel cell catalysts prepared by supercritical deposition: Effect of different precursor conversion routes

Selmi Erim Bozbağ[a], Tolga Gümüşoğlu[b], Serpil Yılmaztürk[b], Christian J. Ayala[c], Mark Aindow[c], Hüseyin Deligöz[b], Can Erkey[a,d,*]

[a] Department of Chemical and Biological Engineering, Koç University, 34450 Sariyer, Istanbul, Turkey
[b] Department of Chemical Engineering, Istanbul University, 34320 Avcilar, Istanbul, Turkey
[c] Department of Chemical, Materials and Biomolecular Engineering, Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA
[d] Koç University TÜPRAŞ Energy Center (KUTEM), Koç University, 34450 Sariyer, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 24 May 2014
Received in revised form 14 August 2014
Accepted 15 August 2014
Available online 23 August 2014

Keywords:
Supercritical deposition
Platinum
Nanoparticles
Cyclic voltammetry
Fuel cell

ABSTRACT

Supercritical deposition (SCD) is used to prepare carbon-supported Pt nanoparticles as electrocatalysts for proton exchange membrane fuel cells (PEMFCs). Dimethyl(1,5-cyclooctadiene)platinum(II) (Pt(cod)me_2) is adsorbed from supercritical carbon dioxide ($scCO_2$) solutions onto Vulcan VX-72 at 13.2 MPa and 50 °C. The adsorbed metal precursor is converted to its metal form via three different routes: thermal conversion in N_2 at ambient pressure (route 1), thermal conversion in $scCO_2$ (route 2), or chemical conversion in H_2 at ambient pressure (route 3). Sequential SCD is used in routes 1 and 3. The mean diameters of the synthesized Pt nanoparticles are smallest for route 1 and largest for route 3. Nano-scale morphology of the electrocatalysts is characterized using transmission electron microscopy (TEM), revealing narrower Pt particle size distributions for the catalyst prepared via route 1 than for those synthesized by routes 2 and 3. Electrocatalyst prepared using route 1 showed the best performance both in specific activity (measured via cyclic voltammetry) and in PEMFC tests among electrocatalysts prepared using different routes.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are emerging devices for electricity generation. PEMFCs operate at higher efficiencies as compared to internal combustion engines due to the direct conversion of chemical energy to electricity. However, there are several factors that have inhibited their more widespread utilization including: the absence of a H_2 infrastructure, relatively high cost of the membrane electrode assemblies (MEAs), and fuel processing requirements [1,2].

Carbon-supported Pt has been the catalyst of choice [3–5] because of its activity for the O_2 reduction reaction (ORR) and H_2 oxidation reaction (HOR) in PEMFCs. These electrocatalysts are conventionally prepared using wet/pore volume impregnation [6], ion-exchange [7], and micro-emulsion based routes [8]. Various carbon supports have been used for this purpose including carbon blacks [9,10], carbon nanotubes [11,12] and activated carbons [13]. Carbon blacks are the materials used most extensively since they are inexpensive with good electrical conductivity and high corrosion resistance.

An alternative method that has been under development for the preparation of supported nanoparticles is supercritical deposition (SCD) [14–20]. SCD consists of dissolution of a metal precursor in a supercritical solvent, the adsorption of the precursor from the supercritical fluid phase onto the surface of the substrate, and the conversion of the precursor to its metal form on the surface of the substrate using various routes [21,22]. This approach leads to well-dispersed nanoparticles with controllable particle sizes [21,23–26]. SCD has been shown to be a very powerful technique for the preparation of supported nanoparticles with excellent control of loading, particle size and distribution [18,21]. In SCD, the metal loading on the substrate can be controlled thermodynamically by using the adsorption isotherm of the metal precursor–substrate system [24,27–32]. The maximum loading is also governed by the

---

* Corresponding author at: Department of Chemical and Biological Engineering, Koç University, 34450 Sariyer, Istanbul, Turkey. Tel.: +90 212 3381866; fax: +90 212 3381548.
E-mail address: cerkey@ku.edu.tr (C. Erkey).

http://dx.doi.org/10.1016/j.supflu.2014.08.014

adsorption isotherm unless an in situ precursor conversion route is followed [21] or multiple adsorption and conversion cycles are applied. Here we refer to the latter approach as “sequential SCD”.

Electrocatalysts prepared using SCD were shown to be very promising for fuel cell applications [33–40]. In particular, Pt/C electrocatalysts prepared using SCD were shown to be very promising catalysts toward the ORR and HOR [35] in voltammetry tests due to the small particle size, homogeneous dispersion, and narrow particle size distribution of the Pt on the carbon support. It has been shown that the conversion method employed during SCD can have a dramatic effect on the physical and chemical properties of the final catalyst. Saquing et al. demonstrated that conversion in a hydrogen atmosphere caused the average size of carbon aerogel-supported Pt nanoparticles to increase by a factor of 2 compared to those produced by thermal conversion [21]. In subsequent work by Bayrakceken et al. the activities of Pt/Vulcan electrocatalysts produced using SCD with different conversion routes were investigated using cyclic voltammetry [27]. The Pt nanoparticle size was found to be 1.2, 1.3 and 2 nm and electrochemical surface area of catalysts was 173, 125 and m^2/g, for catalysts with Pt loading of 9, 15 and 35 wt.%, respectively. Although this latter study established a clear correlation between the electrochemical surface area, the Pt loading and the conversion route, electrochemical performance was not evaluated in PEMFC. The effects of various precursor conversion routes employed during the preparation of Vulcan supported Pt at the same loading via SCD using $scCO_2$ on the electrocatalytic behavior and actual PEMFC performance have not been investigated so far.

In this study, Pt/Vulcan electrocatalysts with the same metal loading (20 wt.% Pt) were prepared using SCD via three different precursor conversion routes: thermal conversion in N_2 at ambient pressure (route 1), thermal conversion in $scCO_2$ (route 2), and chemical conversion at ambient pressure in H_2 atmosphere (route 3). Electrocatalysts were prepared using sequential SCD in routes 1 and 3. The physical properties of the catalysts were characterized using infra-red (IR) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltammetry (CV). MEAs were prepared using these catalysts and the performances of these MEAs were tested in PEMFCs.

2. Materials and methods

2.1. Materials

Vulcan XC-72R (Vulcan) was obtained from Cabot International and was heat-treated in a pyrolysis oven at 150 °C for 4 h in N_2 prior to impregnation. The total, mesopore and micropore surface areas of Vulcan were 235, 152.6, and 82.4 m^2/g, respectively [41]. $Pt(cod)me_2$ (99%; molecular weight = 333.3 g mol^{-1}, melting point = 104 °C) was purchased from Strem Chemicals, Inc. Carbon dioxide (99.998%), hydrogen and nitrogen were purchased from Messer Aligaz. Nafion®117 membranes were obtained from Ion Power Company, Inc. (175 μm) with a nominal equivalent weight of 1100 g eq^{-1}. Nafion®117 solution (5%) was purchased from Quintech. Ultra-pure hydrogen and air were acquired from commercial suppliers. Sulfuric acid (95–98%) and hydrogen peroxide (35%) were obtained from Riedel de Haen and used as received.

2.2. Catalyst preparation

Supercritical deposition experiments were carried out in a custom-made 57 ml stainless steel vessel equipped with two sapphire windows 2.5 cm in diameter (Sapphire Engineering, Inc., Pocasset, MA), a T-type thermocouple assembly (Omega Engineering), a pressure transducer (Omega Engineering), a vent line, and a rupture disk assembly (Autoclave Engineers). The vessel was sealed with poly(ether ether ketone) O-rings. For each experiment, a certain amount of $Pt(cod)me_2$ was placed in the vessel along with a stirring bar, and a certain amount of heat-treated Vulcan substrate was placed in a pouch made of filter paper. A stainless steel screen was positioned in the middle of the vessel to separate the pouch and the stirring bar. The system was sealed and heated to 50 °C using a recirculating heater/cooler (Cole Parmer, Model 12108-15). The system was pressurized with CO_2 up to 13.2 MPa using a syringe pump (ISCO, 260D) and kept at these conditions for 12 h. During this process, $Pt(cod)me_2$ dissolved in the $scCO_2$ and was adsorbed onto the substrate due to mass transfer from the fluid phase. Solubility of $Pt(cod)me_2$ in $scCO_2$ at a density of 720 kg/m^3 ranges from 4.5×10^{-4} to 1.32×10^{-3} (in terms of mol fraction) with temperature varying from 40 to 60 °C, respectively [17,42]. The adsorbed $Pt(cod)me_2$ was then converted to elemental Pt via 3 different routes.

Route 1: Thermal conversion in N_2 at ambient pressure

After the system reached adsorption equilibrium in $scCO_2$ during impregnation of the support from the $scCO_2$ phase, the system was depressurized slowly (0.7 MPa min^{-1}) using a needle valve (Autoclave Engineers). The $Pt(cod)me_2$/Vulcan composite was removed from the vessel. Subsequently, $Pt(cod)me_2$ uptake was measured gravimetrically using an analytical balance (AND GR-200, accurate to ±0.1 mg). The impregnated Vulcan was then treated thermally at 200 °C in flowing N_2 (100 cm^3 min^{-1}) for 4 h in a custom-made quartz process tube (internal diameter 3 cm, length 57 cm), which was placed in a tube furnace (model F1125 Thermolyne). Then, the system was cooled to room temperature under flowing N_2. The composite was removed from the process tube and the metal loading was measured from the weight change using an analytical balance. The platinum content in the final catalyst was calculated by considering that all of the $Pt(cod)me_2$ ligands were transferred to the flowing gas stream as a result of the conversion process. In order to increase the Pt loading gradually up to desired value (20 wt.% Pt), SCD was applied two more times as shown in Fig. 1 (i.e. Pt was deposited on as-prepared Pt/Vulcan using SCD). Precursor uptakes or metal loadings were measured gravimetrically after each step.

Route 2: Thermal conversion in $scCO_2$

In the second route, after the system reached adsorption equilibrium in $scCO_2$, the vessel was heated to 120 °C, which caused the pressure to increase to 26.9 MPa. The system was kept at these conditions for 6 h. Subsequently, the vessel was depressurized slowly and allowed to cool. Then, the Pt/Vulcan composite was removed from the vessel. Here again, the Pt loading was measured gravimetrically using an analytical balance.

Route 3: Chemical conversion in H_2 at ambient pressure

The procedure for the third route (Fig. 1) was identical to that for route 1 except that the $Pt(cod)me_2$ conversion was performed chemically in flowing H_2 (100 cm^3 min^{-1}) at atmospheric pressure and at 200 °C. All of the deposition experiments were repeated twice. Metal loading values given in the manuscript are the average of such experiments. Absolute error in loading was ±0.5 wt.%. The catalysts prepared via the first, second and third routes are hereafter referred to as SCC-1, SCC-2 and SCC-3, respectively.