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Catalyst nanoscale assembly from the vapor phase on corrosion resistant supports

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ABSTRACT

The synthesis process, reactive spray deposition technology (RSDT), utilized a jet-flame to produce Pt nanoparticles. The RSDT process bypasses traditional wet chemical routes by simultaneously nucleating the catalyst on a support and sequential deposition of catalyst layer *via* the gas phase. Pt nanoparticles were attached, in the process gas during the time-of-flight, to the surface of several supports. The supports show promising corrosion resistance under the cathode conditions of a proton exchange membrane fuel cell (PEMFC). The supported Pt catalysts were then studied in regards to structure, stability and electrochemical behavior toward the oxygen reduction reaction (ORR) in perchloric acid. Transmission electron microscopy studies showed that the average Pt particle diameter is ∼2.5 nm. The average diameter and distribution of the Pt particles are independent of the support type and a high degree of catalyst dispersion has been achieved on all supports. The greatest surface area and electrochemical mass activity were obtained using Vulcan XC-72R, while a graphitized carbon support produced the highest specific activity. Based on X-ray photoelectric spectroscopy (XPS) measurements, approximately 30% of the surface of the Pt particles is comprised of Pt^{2+}. This oxide coverage does not extend into the bulk and is below the detection limits of X-ray diffraction (XRD). The electrochemical reduction of oxygen exhibits a typical Tafel slope of −65 to −71 mV/dec.

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1. Introduction

1.1. Catalyst function in the membrane electrode assembly (MEA)

Proton exchange membrane fuel cells (PEMFC), in combination with environmentally friendly sources of "green" hydrogen, are widely believed to be the key enabling technologies for a less carbon-constrained world [1,2]. A total of 183 US issued patents are directly related to the fuel cell and 32 companies are now selling 34 different fuel-cell-related products [3]. Asia dominates the fuel cell industry in terms of system shipments with 17,000 in 2011, 69% of the global market [4]. North America led the 2011 MW data with 59.6 MW, just over 50% of the total; Asia followed second with 36%.

Commercialization hinges on oxygen electrochemistry; this biologically and industrially important reaction involves either the electrocatalytic reduction or evolution of molecular O_2 and is the key rate limiting reaction in many renewable energy technologies including metal-air batteries, water electrolysis, and fuel cells [5]. In the oxygen reduction reaction (ORR), O_2 combines with electrons to form a product (*e.g.*, peroxide or water), whereas the oxygen evolution reaction (OER) generates O_2 gas by removing electrons from the reactant. The ORR and hydrogen oxidation reaction (HOR) are both carried out on a carbon-supported Pt electrocatalyst dispersed in the electrode layer. The ORR overpotential is ∼10 times larger than that for H_2 oxidation at the anode. This large overpotential loss is attributed to the sluggish kinetics of the ORR and to coverage of catalytic active sites by anion adsorption of OH^- (from H_2O) or electrolyte species. A preferable catalyst has a high intrinsic activity for the desired reaction (*i.e.*, turnover frequency) and a maximum number of active sites [6].

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Platinum-based catalysts supported on carbon materials (Pt/C) have become the standard catalyst-support choice in PEMFCs; Pt/C also shares a wide range of industrial uses including hydrogenation, hydrogenolysis, reforming and isomerism [7,8]. Once the Pt is anchored to the support the combined components comprise the 'catalyst'. In automotive based PEMFC applications commercialization hinges on the 'catalyst' due to inadequacies in mass activity <0.44 mA/mg$_{Pt}$ and durability <40,000 h. Conventional MEAs require a catalyst layer with finely dispersed Pt nanoparticles supported on amorphous carbon. The catalyst layer is exposed to temperatures upwards of 80 °C, pH < 1, a transient potential 0.4–1 V that results in a dynamic surface oxide coverage, large swings in humidity, and under certain high-current conditions a flooding of the layer with liquid water. Under these conditions corrosion of the carbon support is one degradation pathway leading to poor durability and unacceptable lifetimes hindering further market penetration [9–11].

Discovery of a support comparable to carbon that offers high electrical conductivity; a large surface area; porosity with equivalent micro-, meso- and macroporous features; increased corrosion resistance; and high Pt activity enhancement would represent a breakthrough in attempts to commercialize PEMFCs. A new approach to catalyst assembly at the nanoscale size using a vapor phase deposition onto corrosion resistant supports is discussed in this article. This approach avoids liquid processing, combines catalyst preparation with electrode formation into one-step, reduces waste generation, allows for independent and real-time control of the electrode components (*i.e.*, support, ionomer, and Pt), leads to uniform catalyst coverage, and is amenable to low Pt loading. Understanding the interplay between different types of support, ionomer, and the Pt is of prime importance in improving the activity and durability of PEM catalysts. The objective of this study is to investigate the size of Pt deposited from the vapor phase on a variety of catalyst supports and their corresponding mass activity while keeping the ionomer concentration constant.

Stability of the catalyst is dependent upon successful attachment of the Pt to the support [12] while maintaining a uniform dispersion (*e.g.*, avoiding agglomeration). The catalytic activity of a supported catalyst is heavily dependent not only on the support material (*e.g.*, amorphous carbon, oxygen deficient titania, graphitized carbon, *etc.*) but also the processing routes used to attach the metal and finally the architecture of the catalyst layer. Architecture of the catalyst layer refers generally to the thickness, porosity, and spatial distribution of the components in the formulation.

In this work, a one-step method for producing the Pt catalyst, attaching to different corrosion resistant supports, and then sequentially forming a catalyst layer (directly from the vapor phase) is explored to investigate the stability and ultimately the feasibility in applying the Pt to the support (*i.e.*, anchoring) *via* a non-liquid route. In addition to dispersion of the catalyst onto a well characterized Vulcan XC-72R support, as a benchmark, this work explored alternate materials that exhibit more promising durability. Previous studies by Roller et al. examined the electrochemical performance and microstructure using a high surface area amorphous carbon (EC-300J Ketjen black, S_{BET} = 1400 m^2/g) deposited by RSDT [13].

In this work, the microstructure and oxygen reduction reactivity were examined on the following platinized supports: a highly graphitized carbon (GC) support CRC 2700 L35 (Cabot Corporation, Boston, MA) [14]; a titanium sub-oxide (*i.e.*, Magneli phases) of the general formula Ti$_n$O$_{2n-1}$ (Ebonex® 10015, Atraverda Ltd., Gwent, UK) [15]; and an amorphous carbon with low sulfur and ionic contamination (Vulcan XC-72R, Cabot Corporation, Boston, MA) [16–18]. A review of the literature on deposition processes using different supports [19–21] suggests that catalyst dispersion and agglomeration is dependent not only on the support but also

on the catalyst preparation. For example Wang et al. found that the extent of Pt aggregation could be controlled by use of a surfactant stabilizer during the reduction process and that the size of the colloids could be controlled by the synthesis temperature [19]. Pt agglomeration on GC using the liquid phase is especially challenging due to preference of the deposition for defect sites and not the basal planes of the graphene carbon sheet [22]. Compared to Pt deposition on amorphous carbon the GCs result in larger Pt particle sizes because of the supports smaller specific surface area (*e.g.*, $S_{GC} \sim 150$ m^2/g) [23]. This low surface area leads to difficulty in dispersing the Pt nanoparticles uniformly using conventional preparation methods [23].

Pt catalyst nucleation and growth can be directly related to the surface defects (edges, steps, vacancies, contaminants, hybridization sp^2 or sp^3, *etc.*). Once the support is graphitized, Pt particles distribute predominantly at edges of the graphite surface during the Pt attachment step [24]. Graphitization increases resistance to the loss of the carbon support and hinders Pt sintering since Pt anchors to the π sites (sp^2 hybridized carbons) leading to an increased metal–support interaction [7].

Several reviews of potential support materials have recently been published [25–27] on materials that are alternatives to carbon. Of particular interest are the sub-stoichiometric titanium oxides of the general formula Ti$_n$O$_{2n-1}$ (Magnéli phases), where *n* is a number between 4 and 10 [28,29]. These Magnéli phases are characterized by extended planar defects and crystallographic shear planes which vary according to the oxygen deficiency. Magnéli phases are produced from high temperature reduction of titania in a hydrogen atmosphere and recently have even been produced in lab scale quantities directly by a flame-based process [30]. These bluish-black ceramics exhibit good conductivity (∼1000 S/cm) comparable to that of graphite (∼727 S/cm) [31,32].

The ceramic can be processed into a number of forms, such as tiles, rods, fibers, foams and powders and are of interest in cathodic protection, batteries, catalysts support for fuel cells, treatment of aqueous waste and contaminated water [33]. In addition to exceptional stability under PEMFC operating conditions, there is also a documented strong metal–support interaction (SMSI) between the surface of certain group VIII noble metals (*e.g.*, Pt) and the oxides of certain transition metals (*e.g.*, Ti, Nb, and Ta). This SMSI between Pt and the sub-oxide is due to the unique hypo-hyper-*d*-interbonding and interactive primary (M-OH) spillover, making this support ideal for both water electrolysis and PEMFCs [34]. 2.5–5 wt.% Pt deposited onto Ti$_n$O$_{2n-1}$, with a surface area of 0.95 m^2/g, has been performed by Ioroi et al. using an impregnation method [35]. They found that the onset potential of the corrosion current was much higher than for Vulcan XC-72R [35]. Krstajic et al. [34] prepared a sample of 10 wt.% Pt on Ebonex® through impregnation using Pt(NH$_3$)$_2$(NO$_2$)$_2$ in 2-propanol; the solution was ultrasonically mixed and then dried at 80 °C for 12 h. Reduction in H$_2$ at 300 °C for 2 h changed the platinum salt to Pt metal.

1.2. Catalyst layer architecture and degradation mechanisms

The catalyst-layer architecture at the cathode must function to allow unobstructed access to three ORR process streams consisting of O$_2$ gas, protons (H$^+$) from the electrolyte in the hydrated ionomer, and electrons traveling through the solid carbon support *via* the external circuit. In order to reduce O$_2$ to H$_2$O all three phases must be in physical proximity hence the term "triple phase boundary" in reference to the sites where gas, liquid, and solid are in coincidence. An additional constraint in the architecture is imposed by the liquid H$_2$O products which must be efficiently removed to prevent a condition of flooding whereby the reaction rate is hindered, owing to a 5 order of magnitude drop in O$_2$ diffusion (∼0.2 cm^2/s in gas *versus* 5×10^{-6} cm^2/s in water) to the active sites. The