



Nanoscale analysis of structural and chemical changes in aged hybrid Pt/NbO_x/C fuel cell catalysts



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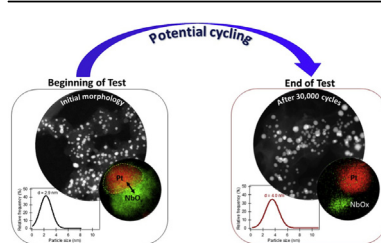
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HIGHLIGHTS

- A Pt/NbO_x/C hybrid fuel cell catalyst has been synthesized.
- The effect of potential cycling on Pt and NbO_x species has been investigated.
- The catalyst meets std. activity and durability requirements.
- Pt has good contact with NbO_x for metal-support interaction.

GRAPHICAL ABSTRACT



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ABSTRACT

We characterize the structural and chemical changes that take place in an electrochemically tested proton-exchange fuel cell cathode material composed of platinum nanoparticles on a niobium oxide-carbon black hybrid support. Two hybrid catalysts with different niobium oxide content (5 wt% and 12 wt%) are compared at the beginning and end of potential cycling. We observe an overall increase in the particle size of the hybrid catalysts after potential cycling, mediated by Ostwald ripening process. The general nanostructure of the catalysts was composed of small Pt-rich particles that were linked to niobium oxide particles. Nanoscale and microscale spectroscopy of the pristine materials reveals several co-existing oxidized forms of niobium (5⁺, 4⁺, 2⁺) in the systems; the most predominant being Nb(V). The study of the energy loss near-edge structure of the Niobium L_{2,3} edge of catalysts after being subjected to accelerated stress test (AST) potential cycles provides clues on the evolution of niobium oxides (NbO_x), in which the relative distribution of Nb(V) decreases, while the number of Nb particles in lower oxidation states slightly increases. Furthermore, energy-dispersive spectroscopy reveals that the content of Nb decreased after cycling, implying that the loss of NbO_x eventually altered the fraction of linked Pt-NbO_x sites. The observed nanoscale catalyst changes and the presence of the NbO_x may have important implications for developing an alternative design for improved hybrid catalyst materials.

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1. Introduction

The biggest challenge facing the commercialization of fuel cell vehicles is finding the best balance of cost, performance, robustness, and durability. Fuel cell technology remains largely based on precious metal catalysis. After decades of research, platinum (Pt)

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based nanoparticles on a conductive carbon supports are the most commonly used catalysts due to their exceptional performance when compared to other materials, and Pt based catalysts can contribute up to 30% of the total fuel cell stack cost [1]. Catalyst durability is one of the main issues determining the viability of these materials in commercial solid polymer electrolyte fuel cell stacks [2]. For this reason, reducing the platinum loading to a minimum is of utmost relevance for stack cost reduction.

High fuel cell performance can be maintained with a lower Pt loading by increasing the Pt specific activity (SA) or by increasing the degree of Pt utilization. The specific activity of Pt electrocatalysts can be enhanced through what is known as the Strong Metal Support Interaction (SMSI) [3], either with a carbon support [4] or with an early (refractory) transitional metal oxide (TMO) support [5,6]. The TMO support leads to profound changes in the catalytic and chemisorption properties and the morphology of the Pt metal particle [7]. The presence of such reducible oxides is believed to play a critical role in enhancing Pt oxygen reduction reaction activity (ORR) important for solid polymer electrolyte fuel cells [8]. For instance, Pt deposited on TMO such as NbO_x ($X = 1, 2, 2.5$) has been shown to exhibit 2–3 times higher ORR activity [9–11]. The mechanism of metal oxide participation in the ORR is still under debate. Some believe that NbO_x prevents population of the Pt surface with hydroxyl ions in aqueous solutions, thereby facilitating O_2 adsorption on the Pt surface [9]. Others propose that oxygen molecule dissociative adsorption takes place on metal oxides when it is in contact to Pt [12].

Along with high activity, high durability is necessary for Pt catalysts subjected to the harsh environment inside a fuel cell for automotive applications. Amongst the degradation mechanisms, platinum dissolution and redeposition, sintering or agglomeration, and detachment promoted by carbon corrosion, have all been linked to a decrease in catalytic activity resulting in a loss of performance and ultimately to reduced durability [13]. In this context, it has been hypothesized that the use of TMOs as a support component anchoring Pt nanoparticles results in reduced Pt agglomeration [14]. However, TMO supported Pt catalysts have low surface area, low electronic conductivity and low porosity leading to lower performance, especially in high current density region [12]. In comparison, high surface area (HSA) carbon support materials have higher electrical conductivity, higher porosity, and higher connectivity to the gas diffusion media. For this reason, the use of HSA carbon support materials as templates for Pt/ NbO_x system would combine the advantages of TMO and HSA carbon properties. Although these modifications to the support material are promising, there are limited studies on the catalyst structure and possible understanding of the mechanisms at the source of these effects as applied to fuel cell catalysis.

In the studies described herein, we examined a series of catalysts containing Pt nanoparticles supported on a niobium oxide hybrid carbon support prepared by the sol-gel technique. Furthermore, an atomic scale insight into the evolution of the structure and composition of the system after accelerated electrochemical cycling tests, using advanced electron microscopy techniques including High Resolution Transmission Electron Microscopy (HREM), High Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM), Energy Dispersive X-Ray Spectroscopy (EDX), and Electron Energy Loss Spectroscopy (EELS), is provided. We observe a complex heterogeneous nanostructure in which the active phase is present either as a Pt-Nb alloy phase, or Pt-rich and non-alloyed Pt linked to NbO_x particles. Additionally, X-ray photoelectron spectroscopy (XPS) was used to understand the oxidation state of Nb in as-prepared hybrid catalysts. For comparison, we also provide the nanoscale analysis needed to understand the reducibility and evolution of the oxidation state of NbO_x after

cycling test. Ex-situ electrochemical measurements demonstrate increased activity coupled with good stability after being subjected to accelerated stress test (AST) potential cycles compared to Pt baseline.

2. Experimental

2.1. Synthesis of hybrid catalysts

Samples of “hybrid catalysts” have been prepared in two steps as discussed in previous studies [15]. Briefly, NbO_x was deposited on dry carbon through the sol-gel technique using niobium Ethoxide ($\text{Nb}(\text{OEt})_5$) as the precursor. The dry NbO_x/C solid was mixed with Platinum (II) 2,4-pentanedionate and ball milled for 1 h followed by thermolysis treatment. First, the sample has been subjected to a treatment at 400 °C in a flow of Ar and then at 800 °C in a mixture of 10% H_2/Ar gas for 1 h, followed by fast cooling up to room temperature. The technique provides the selective interaction of Pt particles with NbO_x .

Oxidized small acetylene black (OSAB) supplied by Denka (BET surface area of 800 m^2/g) has been used as high surface area carbon support. The synthesized catalysts contain different amounts of NbO_x and Pt/Nb atomic ratio varied from 0.1 to 4.0:1. The Pt crystallite particle size has been determined by XRD analysis.

In order to gain insight into the chemical and crystallographic nature of the niobium oxide, a reference material containing only NbO_x phases has been synthesized in the absence of Pt precursor using activated carbon Darco G60 (Norit Co) for XRD and EELS measurements. Experimentally, we found that this kind of support provides higher amounts of reduced forms of Nb. Localized EELS and XRD measurements recorded from Nb-rich grains were used as reference, along with data obtained from analysis of commercial bulk oxides of NbO , NbO_2 , and Nb_2O_5 .

2.2. Electrochemical catalyst testing

Electrochemical evaluation of hybrid catalyst was performed both ex-situ, using a Thin Layer Rotating Disk Electrode (RDE) technique [16–18]. The surface area of the glassy carbon electrode was 0.196 cm^2 . The tests were performed in 0.09 M ($\text{pH} \approx 1$) sulfuric acid and 0.1 M ($\text{pH} \approx 1$) perchloric acids. Electrochemical surface area (ECSA) was determined from cycling voltammograms in N_2 saturated electrolyte and specific activity (SA) and mass activity (MA) were taken from potentiodynamic experiments in O_2 saturated electrolyte. In the following, mass activity, in A/g of Pt based on the nominal Pt loading, was determined from ORR curves at 0.9 V on anodic sweep at 2000 r/min at scan rates 5 mV/s, using the following equation:

$$i_k/\text{Pt loading g}/\text{cm}^2$$

where: i_k – kinetic current density determined from: $i_k = \frac{i^*i_D}{i_D - i}$

i_D – limiting current density at ~ 0.25 V;
 i – measured current density taken at 0.9 V.

Usually Pt loading was around 10 $\mu\text{g}/\text{cm}^2$.

Electrocatalytic surface area (ECSA) in m^2/g of Pt was determined from the unalternated CV curves and corresponds to the Pt area desorbing hydrogen from 0.05 to 0.4 V and normalized on Pt loading.

The data on MA and ECSA were used to calculate specific activity (SA) of evaluated catalysts A/ m^2 Pt. All catalysts were subjected to accelerated stress test (AST) both in 0.09 ($\text{pH} \approx 1$) sulfuric acid and 0.1 M ($\text{pH} \approx 1$) perchloric acid saturated with N_2 . Square Wave

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