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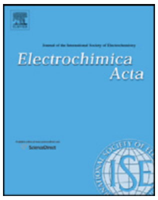

# Effects of synthesis condition on formation of desired crystal structures of doped-$TiO_2$/carbon composite supports for ORR electrocatalysts

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ABSTRACT

The composite supports, $(Nb_{0.07}Ti_{0.93}O_2)_{25wt\%}–C_{75wt\%}$ and $(Nb_{0.07}Ti_{0.93}O_2)_{70wt\%}–C_{30wt\%}$, as well as their supported Pt–Pd alloy electrocatalysts, 20 wt%$Pt_{0.62}Pd_{0.38}/((Nb_{0.07}Ti_{0.93}O_2)_{25wt\%}–C_{75wt\%})_{80wt\%}$ and 20 wt%$Pt_{0.62}Pd_{0.38}/((Nb_{0.07}Ti_{0.93}O_2)_{70wt\%}–C_{30wt\%})_{80wt\%}$ for oxygen reduction reaction (ORR), are synthesized, respectively, using an acid-water based solution as solvent. The effects of three factors, namely concentration of HCl, the ratio of titanium precursor to solvent, and the ratio of metal-oxide to carbon in the composite support, on the $TiO_2$ anatase-to-rutile transition are investigated in an effort to optimize the supports and their supported catalysts with respect to both ORR catalytic activity and durability. Based on both the high ORR activity and durability, these catalysts should be feasible if used in PEM fuel cells as cathode electrocatalysts.

## 1. Introduction

At the current state of technology, the most practical electrocatalysts for the oxygen reduction reaction (ORR) in proton-exchange membrane (PEM) fuel cells are nanoparticles of platinum (Pt) and Pt alloys supported on carbon substrates (abbreviated as Pt/C and Pt-M/C, respectively) [1,2]. Carbon as a support is superior due to its high surface area and high electronic conductivity [3]. However, Pt/C catalysts encounter stability issues when a fuel cell is operated at voltages above 0.9 V because of the well-known carbon corrosion reaction:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-, \quad E^o = 0.207\,\text{V vs. SHE} \qquad (1)$$

The mitigation of this problem has been proposed using either graphitized carbon or carbon nanotubes or replacing the carbon with metal oxide including $TiO_2$. It is believed that a metal oxide as a possible support for PEM fuel cell applications could enhance both the activity and durability through catalyst-support interaction [3,4], leading to the increased fuel cell ORR performance [5–7].

Fully replacing the carbon support with metal oxide however is not viable. For instance, compared to carbon materials, metal oxides show relatively low electronic conductivity, limiting the electrochemical transportation of electrons between electrode and catalyst particles. Therefore, metal oxides alone may not be practical catalyst supports. The effective way to alleviate the challenges for such support is to combine the advantages of both carbon and metal oxide to make composite materials. Therefore, another class of support emerged recently as composite supports (carbon + metal oxide).

As a typical metal oxide, $TiO_2$ (also called titania) has been widely used in many areas; such as photovoltaic cells, photocatalysis for water splitting, liquid-junction dye-sensitized solar cell (DSSCs), optics, charge storage as well as antimicrobial applications [8–12]. It exists in three crystalline forms: anatase, rutile and brookite. For $TiO_2$ with nanostructure, its anatase phase is metastable and thermodynamically favorable under the as-prepared condition. Its rutile phase is relatively more stable than anatase phase. However, rutile phase can only be formed by controlled synthesis conditions or by heat treatment at a temperature above 700 °C [13]. Rutile and anatase $TiO_2$ phases have their unique properties. For example, nanosized anatase $TiO_2$ exhibits superior photocatalytic activity vs. rutile [14,15] while the rutile $TiO_2$ has relatively high electronic conductivity and high strength and resistance to corrosion. Therefore, successful control of the synthesis of

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$TiO_2$ and its analogs with desired crystal structure represents technologically important processing. In order to further increase the conductivity of $TiO_2$, doping with metal such as niobium (Nb) seems a promising strategy [7,16]. However, even using rutile phase and metal-doped $TiO_2$, the conductivity is still not high enough to allow for use as an electrocatalyst support. As mentioned above, combining doped-$TiO_2$ with carbon to make a composite support seems a promising way to design highly durable supports for PEM fuel cell ORR catalysts. Carbon and metal oxide together may have several advantages as follows: (1) Carbon addition could increase the bulk conductivity and surface area of support, (2) Metal oxide could enhance the catalyst-support interactions, and (3) Me-doped–$TiO_2$ (Me = transition metals) in rutile phase could enhance the localized electronic conductivity and the strength of the crystal structure, facilitating both electrochemical performance and durability of electrocatalytic activities. Even though, carbon in the composite can be oxidized depending on its concentration, compared to a pure carbon support, the corrosion rate of the entire composite should be lower.

Regarding the $TiO_2$-based support, there are two ways to do optimization, i.e. structural (anatase-to-rutile transition) and compositional (transition metal doping of $TiO_2$). Controlling anatase-to-rutile transition is important for structural stabilization. For PEM fuel cell applications, it is desirable to obtain the more durable and conductive $TiO_2$ rutile phase since anatase is metastable and is subject to phase changes when surrounding conditions alter. On the other hand, compositional modification, for example, doping of $TiO_2$ by introducing other elements into the $TiO_2$ framework is a practical way to tailor both physical and chemical properties. In addition, doping could enhance both the structural stability and electronic conductivity of the rutile form.

There are several factors influencing the anatase-to-rutile transition such as cation addition [17], critical-nuclei-size, packing density and coordination of primary particles in the aggregate [18].

Many studies prove that dopants from group-V elements, such as Nb, for $TiO_2$ can be substitutionally incorporated within the structure lattice to form a solid solution with $TiO_2$ [6,7,16,19,20]. In general, cations such as Nb(V) addition can stabilize $TiO_2$ in anatase phase and raise the anatase-to-rutile transition to higher temperature, as suggested by Chhina et al. [17]. On the other hand, introducing the transition metals into the $TiO_2$ framework could increase electronic conductivity as well. High-resolution core- and valence-level photoemission spectra indicate that at low doping levels, Nb(V) in the $TiO_2$ rutile lattice could generate a new electronic state that is associated with Ti(III) ions [16]. Therefore, doping could cause increased electronic conductivity in the newly formed structure. Moreover, some studies also showed that doped-$TiO_2$ could enhance the crystalloid structure of metal oxide, further stabilizing the chemical and physical properties of materials [9,12,21].

Kumar et al. [18] proposed the concept of critical-nuclei-size and packing density of metal oxide to understand the mechanism of anatase-to-rutile transition. This study showed that the anatase-to-rutile transformation could be greatly suppressed if the particles did not grow into the critical-nuclei-size. Reaching of critical-nuclei-size could be affected by particle packing density and coordination during a synthetic process. The low packing density of particles likely prevents the growth of particles into large size, and stabilizes the anatase phase, therefore raises the transition temperature of anatase-to-rutile transition. Other work [22] revealed that if the synthesis was carried out in an alcohol-based solvent, the packing density of particles was lower compared to synthesis in water-based solvent, leading to a small particle size of metal oxide. In the case of alcohol-based synthesis, the transformation of anatase-to-rutile only occurred when the resulting materials were heated to high temperatures (>700 °C), at which the metal oxide particles were activated to grow to a size that was over the critical-nuclei-size, facilitating the anatase-to-rutile transition. High temperature treatment can significantly reduce the specific surface area of materials. In order to retain the large surface area of $TiO_2$-type supports, it is desired to produce a well-defined rutile structure in the "as-prepared" condition, free of any need for retreatment. In this regard, the proper chemistry routes should be chosen. Many studies report the synthesis of $TiO_2$ by wet chemistry, with the process carried out in solution. Among them, acid-water based solvent, such as HCl, has proved to be an effective solvent for synthesizing $TiO_2$-type compounds. Wang et al. reported the synthesis of the Nb-doped $TiO_2$ supports in a mixture of alcohol- and acid-based solutions [23], resulting in the high conversion rate of anatase to rutile phase after heat treatment. It was also observed that when Pt particles were deposited on such a support, a better catalyst-support interaction could be achieved [24]. In addition, Me-doped $TiO_2$ hybrid supports contain a number of different elements; each of which can influence the structures and properties of the support matrix in a different way. For example, both cation and carbon additions would stabilize the anatase phase. Some studies show that anatase phase and graphitic layers on the surface of $TiO_2$ could suppress other phase formations of $TiO_2$ even at temperatures higher than 900 °C [15].

In an effort to develop more durable ORR catalysts for PEM fuel cell applications, the composite support combining carbon and Nb-doped $TiO_2$ with their supported Pt–Pd alloy catalysts was synthesized, and the optimization of composition and synthesis parameters were carried out. The variables of synthesizing the composite supports, such as the concentration of HCl aqueous solution, the relative amount of titanium precursor in solvent and the percentage of metal-oxide in the composite support, were studied individually and their effects on the structure formation of doped-$TiO_2$ were also identified. Electrochemical performances (both ORR mass activity and durability) of the composite supported $Pt_{0.62}Pd_{0.38}$ catalysts are reported in this paper.

## 2. Experimental

Composite supports were synthesized using HCl as a solvent. 37% HCl (Sigma–Aldrich) was diluted to the desired concentrations by deionized water (D.I. water). Titanium (IV) iso-propoxide (Alfa Aesar), niobium (V) ethoxide (Alfa Aesar), chloroplatinic acid hexahydrate ($H_2PtCl_6$, Sigma–Aldrich) and ammonium hexachloro palladate (IV), ($Pd(NH_4)_2Cl_6$, Sigma–Aldrich) were used as received without further purification. Carbon black TKK-E (TKK, Japan) was selected as the carbon component for the synthesis of composite supports.

In a typical synthesis for composite materials, TKK-E carbon was first mixed in the desired concentration of HCl aqueous solution, which was ultrasonicated for 1 h followed by stirring for 1 h to form a carbon suspension. Then, the desired amount of titanium, and niobium salts were dissolved in a separate HCl solution and then stirred for another 1 h to form the precursor solution. This precursor solution was drop-wise added into the carbon suspension with stirring. The formed mixture was refluxed at 120 °C under stirring for 16 h. The resulting powder was then washed with D.I. water until pH 7 was achieved using a glass Millipore vacuum filtration set-up and then dried at 80 °C in air. The final products were ground to form a dry powder. If heat-treatment was required, this powder was put into the furnace and heat-treated in $H_2$/Ar at desired temperature and time. The formed composite materials are designated as $(Nb_{0.07}Ti_{0.93}O_2)_{Y\mathrm{wt}\%}$–$C_{(1-Y)\mathrm{wt}\%}$, ($Y$ = 25–75 (weight)) throughout this paper.

For Pt–Pd alloy catalyst synthesis, an intermittent microwave heating (IMH) assisted polyol method was employed to deposit