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TiO_2–RuO_2 electrocatalyst supports exhibit exceptional electrochemical stability

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ABSTRACT

Titanium dioxide–ruthenium dioxide (TiO_2–RuO_2; TRO) powders were prepared in both the hydrous and anhydrous form using a wet chemical synthesis procedure. These materials were characterized by XRD, TEM, and BET. Their electrical conductivity and electrochemical properties such as stability under potential cycling, electrochemical surface area (ECSA), electrocatalytic activity, and fuel cell performance were measured. Anhydrous TiO_2–RuO_2 (TRO-a) demonstrated exceptional electrochemical stability compared to baseline Vulcan XC-72R carbon when tested using an aggressive accelerated stability test (AST) protocol. The various TRO powders were catalyzed by depositing platinum nanoparticles by an impregnation–reduction method to yield Pt/TRO electrocatalysts. The Pt/TRO-a electrocatalysts had a mass activity of 54 $\mathrm{mA\,mg_{Pt}^{-1}}$ and a specific activity of 284 $\mathrm{\mu A\,cm_{Pt}^{-2}}$ for the oxygen reduction reaction. Fuel cell polarization data was obtained on membrane electrode assemblies (MEAs) prepared with Pt/TRO and baseline Pt/C electrocatalysts showed that the Pt-TRO-based MEAs exhibited very good performance. The performance obtained was below the Pt/C benchmark, however, further improvements in performance are expected with greater optimization of the Pt particle size and electrode structure.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) have the potential to serve as efficient, environment friendly and modular electrochemical energy conversion devices with applications in the automotive, stationary power, and portable/military sectors. Over the past several years, much research has been focused on improving the performance of PEFCs and their constituent components [1–4]. One of the key remaining challenges is the enhancement of PEFC component durability and reliability [5]. Presently, the most widely used electrocatalyst in PEFCs membrane electrode assemblies (MEAs) is platinum supported on high surface area carbon [6]. However, the carbon support has limitations in terms of its electrochemical stability. Electrooxidation of the carbon support (i.e., carbon corrosion) can occur during fuel cell operation. The reaction rate for the electrooxidation of carbon can increase dramatically under certain transient operating conditions (e.g., PEFC start-up/shut-down; fuel starvation) [7]. The local electrode potential at the cathode and/or the anode can escalate up to 2 V under these conditions, resulting in an extremely large overpotential (and hence reaction rate) for the carbon electrooxidation reaction [8]. The consequent irreversible loss of carbon causes the release of attached platinum particles. These particles become electrically isolated, leading to lower Pt utilization as well as a marked degradation in fuel cell performance [9,10]. Carbon corrosion also causes the agglomeration and sintering of Pt particles, leading to a loss in the electrochemically active surface area (ECSA) of the PEFC electrode [11]. To address the issue of catalyst support corrosion, much effort has been devoted to developing more stable carbon materials, some with higher graphitic character, such as carbon nanotubes [12,13], nanocoils [14,15], nanohorns [16], nanofibers [17,18] and graphene [19]. However, most of these carbon materials are still susceptible to corrosion at high electrode (over)potentials [20]. Various alternative non-carbon catalyst support materials have been investigated, including SnO_2 [21,22], ITO [23], WO_x [24,25], TiO_2 [26,27], RuO_2 [28,29], SiO_2 [30,31], and WC [32,33]. Some of the metal oxide supports have been shown to act as a co-catalyst and thereby enhance the activity of the supported electrocatalyst [34–38].

For example, RuO_2–TiO_2 has been used as a candidate material for dimensionally stable anodes [39,40]. This material was found to demonstrate high electrical conductivity and also demonstrated high chemical stability in acidic and oxidative environments [39,40]. Recently, RuO_2–TiO_2 binary oxides have also been used as a catalyst support for fuel cell applications. Haas et al. [26] reported that $Pt/Ru_xTi_{1-x}O_2$ catalysts had an ECSA, as measured by cyclic voltammetry in a half-cell configuration, comparable to that of commercial carbon supported catalysts. However, no stability and fuel cell performance testing of these materials was

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conducted/reported by the authors. Huang et al. demonstrated that TiO_2, when used as a catalyst support, exhibited excellent stability and fuel cell performance [41]. The ECSA of the Pt/TiO_2 electrocatalyst decreased by only about 20% after the potential was held at 1.2 V for 80 h, as compared with a 93% loss in ECSA in a baseline Pt/C catalyst after a similar test. However, the stability and conductivity of the stand-alone support was not reported. The use of hydrous RuO_2 as an electrocatalyst support in fuel cells has also received attention due to its mixed-conducting properties [42]. Prior research has shown that Pt/$RuO_2{\cdot}xH_2O$ possesses higher electrocatalytic activity toward methanol oxidation compared with PtRu black [29]. More recently, Ho et al. [43] synthesized $Ti_{0.7}Ru_{0.3}O_2$ as a co-catalyst support for Pt. The $Ti_{0.7}Ru_{0.3}O_2$ support was shown to induce electronic interactions with the metal particles, leading to an enhancement of CO-tolerance, catalytic activity, and durability due to both the strong metal-support interactions and the high proton conductivity of hydrated $Ti_{0.7}Ru_{0.3}O_2$. Both direct methanol fuel cells (DMFCs) and PEFCs with Pt/$Ti_{0.7}Ru_{0.3}O_2$ catalyst as anodes demonstrated better performance than their counterparts with a baseline Pt/C catalyst. This study did not report any stability data or use of these catalysts at the cathode, which is the electrode experiencing excursions to high potentials during fuel cell operation.

Carbon corrosion can occur at both the anode and cathode during fuel cell start-up/shut-down and under fuel starvation conditions [7]. Merely studying the change in ECSA of a catalyzed support does not in itself provide any indication of stand-alone support stability. Therefore, in this work, the stability of the catalyst supports was evaluated independently from that of the supported electrocatalyst. Moreover, the MEAs prepared in this study used Pt/TiO_2–RuO_2 catalyst at both the cathode and the anode. The possibility of enhancing the performance of the PEFC by utilizing hydrous RuO_2 catalyst supports that conduct both protons and electrons on their surface was also evaluated.

In this study, TiO_2, a semiconductor known to be corrosion resistant in acidic and oxidative environments [27,41], was synthesized with high BET surface areas and tailored porosities. The role of TiO_2 in this study was to serve as a corrosion resistant, high surface area template for the final electrocatalyst support. Titanium dioxide–ruthenium dioxide powders in hydrous (TRO-h) and anhydrous (TRO-a) forms were prepared using a wet chemical synthesis procedure. The physical and electrochemical properties of this non-carbon support were systematically measured in both non-catalyzed and catalyzed forms.

2. Experimental

2.1. Reagents

The following chemicals were used as received: titanium(IV) oxide (TiO_2, Aeroxide P25, Acros Organics), ruthenium(III) chloride hydrate ($RuCl_3{\cdot}xH_2O$, 35–40% Ru, Acros Organics), chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, ACS reagent, ≥37.50% Pt basis, Sigma–Aldrich), formic acid (HCOOH, ~98%, Fluka), sodium hydroxide (NaOH, ACS, Fisher), hydrogen peroxide (H_2O_2, 35 wt% solution in water, Acros Organics), 5 wt% Nafion® (1100 EW) (Solution Technologies, Mendenhall, PA). All aqueous solutions were prepared with 18.2 MΩ deionized water from a Millipore water system.

2.2. Preparation of TiO_2–RuO_2

TiO_2–RuO_2 powders were prepared by a simple wet chemical procedure [44]. In a typical synthesis, 12.5 mmol TiO_2 was dispersed in 250 mL DI water and sonicated for 30 min. 12.5 mmol $RuCl_3{\cdot}xH_2O$ was added into the mixture under stirring for 30 min. 0.05 N KOH(aq) was then dropped into the mixture under stirring until the pH of the solution reached 7. The black powder obtained was filtered out and washed repeatedly with deionized water. The powders were then dried at 120 °C for 8 h to yield hydrous TiO_2–RuO_2 (TRO-h). A portion of the TRO-h was further calcined at 450 °C for 3 h in air to yield anhydrous TiO_2–RuO_2 (TRO-a).

2.3. Preparation of 40 wt% Pt/TiO_2–RuO_2 electrocatalysts

Platinum nanoparticles were synthesized by the chemical reduction of Pt precursor with formic acid [45]. In a typical synthesis, a suspension of 5 mmol TRO-a or TRO-h support in reaction solution (1.9 mmol $H_2PtCl_6{\cdot}6H_2O$ and 30 mL HCOOH in 600 mL of water) was sonicated for 30 min. The suspension was heated at 80 °C for 2 h under vigorous stirring. The product obtained was collected by vacuum filtration and washed several times with deionized water, and then dried in an oven at 60 °C. For selected samples, additional heat treatment was conducted at 200 °C and 450 °C. The catalyst obtained was denoted as Pt/TRO-a-*b*, where *b* represented the annealing temperature to which the catalyst was exposed.

2.4. Characterization techniques

X-ray diffraction (XRD) was performed using a Rigaku Miniflex diffractometer to confirm the presence of ruthenium oxide and platinum and to estimate platinum crystallite size. Diffractograms were recorded in the range $2\theta = 20$–80° with a step of 2 min/degree.

Transmission electron microscopy (TEM) was used to determine the size and distribution of the platinum particles and support aggregates. TEM micrographs were obtained using a Jeol 2100F microscope equipped with a liquid nitrogen Si (Li) EDX detector, at an acceleration voltage of 200 kV.

A Brunauer–Emmett–Teller (BET) surface area analyzer was used to calculate the BET specific surface area by a multipoint analysis of nitrogen desorption isotherms.

The two-point probe technique was used in conjunction with linear-sweep voltammetry to measure the electrical conductivity of the supports. All experiments were conducted at room temperature and were performed on pellet samples using a Gamry potentiostat. Sample preparation and other experimental details are provided in the corresponding supporting information section.

2.5. Evaluation of electrochemical surface area (ECSA)

Electrochemical characterization was performed in a three-compartment electrochemical cell containing 0.1 M $HClO_4$ as the electrolyte. A glassy carbon disk ($0.196\ cm^2$) was used as the platform upon which the active material was deposited to yield the working electrode; a saturated calomel electrode (SCE) was used as the reference electrode; a Pt foil was used as the counter electrode. Details about ink and electrode preparation are provided under supporting information.

The electrolyte was purged with nitrogen gas for 30 min before the measurement. Due to minor contamination from the binder, the electrode potential was cycled 20 times at a scan rate of 100 mV/s between 0.05 and 1.2 V (vs. NHE) to produce a clean surface. Subsequently, a cyclic voltammogram (CV) was measured by scanning the working electrode potential between 0.05 and 1.2 V at a scan rate of 20 mV/s.

The ECSA was calculated by measuring the charge associated with hydrogen desorption (C) between 0.05 and 0.4 V and assuming $210\ \mu C\ cm^{-2}$ as the conversion factor corresponding to the charge associated with the adsorption of one monolayer of hydrogen on