



Elaboration and characterization of ruthenium nano-oxides for the oxygen evolution reaction in a Proton Exchange Membrane Water Electrolyzer supplied by a solar profile



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ABSTRACT

Highly crystalline rutile-like structure ruthenium oxide material was synthesized from the hydrolysis method. A heat-treatment procedure was effective to recover catalyst powders free from organic carbon species which could be resulted in the traces of ethanol as solvent. Voltammetry (CV and LSV) and electrochemical impedance spectroscopy (EIS) were used to determine the capacitance and the kinetic parameters of the RuO₂ anodes for the oxygen evolution reaction (OER). The utilization of this catalyst as anode in a single cell PEM electrolyzer has shown high activity toward pure H₂ and O₂ gases production. Exchange current density and Tafel slope of 3.3 10⁻⁸ A cm⁻² and 51 mV dec⁻¹, respectively determined at 60 °C, showed that the H₂O oxidation to O₂ was limited by intermediate species formation step. During the durability tests in a 25 cm² single PEM water electrolyzer (PEMWE) supplied by a solar power profile, the area resistance was raised in the 300–345 mΩ cm² range and an efficiency loss of 330 μV h⁻¹ was measured from 1.85 V at 1 A cm⁻² and 80 °C.

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1. Introduction

The current increasing world demand on energy is a most concerning problem because the excessive utilization of fossil fuels as primary energy sources is not sustainable [1]. Moreover, the greenhouse effect is largely correlated to this utilization for industrial processes and hydrocarbons combustion. The regulation of the demand on energy drives the important research projects so as to establish new energy vectors such as hydrogen. Hydrogen can be used as a conventional fuel either burned to provide energy or converted into electricity in proton exchange membrane fuel cell (PEMFC). Water electrolysis represents the best means for the clean hydrogen production [2]. It can be realized in alkaline or acidic media; the second medium presents some advantages as greater safety, lower energy consumption, and possibility of operating at higher current densities. The proton exchange membrane water electrolyzer (PEMWE) permits to produce pure oxygen and hydrogen without by-product [3]. Water is split to oxygen,

electrons and protons at the anode. The produced protons migrate through the membrane to the cathode, to be reduced to hydrogen gas. It is well-known that the cathodic reaction in water electrolyzer catalyzed by platinum nanoparticles occurs easily with low overpotential [4,5], while the anodic reaction so-called oxygen evolution reaction (OER) requires largest overpotential. The performance of a PEMWE depends on the structure and the efficiency of the anode catalyst. In the PEMWE, the main source of efficiency loss has been identified to be the competition between water adsorption and oxygen desorption. Indeed, according to the literature, these adsorbed species might block the active sites during a multi-step reaction [6,7]. Therefore, the development of efficient catalysts toward OER is a challenging task. Several studies have shown that the most efficient electrocatalysts for OER are noble metal and noble metal oxide electrodes [8]. As anode materials, oxides are particularly interesting due to their greater stability at high potentials compared with metals toward the water oxidation reaction. Many studies correlating metal oxides structure and their electrochemical activity for water splitting have been reported [9,10]. Ruthenium oxide (RuO₂) and iridium oxide (IrO₂) were the most studied, ruthenium being the most active catalyst for O₂ production [11–14].

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Ruthenium oxide may be chemically or physically synthesized by sol-gel method [15], colloidal [16] and Pechini methods [17], pulse laser deposition [18] or radio frequency (RF) magnetron sputtering [19]. Despite all the interest focused on RuO₂, the price of metal precursors and the cost of production of the materials are still very high. In this work, we report a new synthesis method of metal oxides by hydrolysis of chloride precursors in ethanol medium that allows to minimize this price, in comparison with the method of thermal decomposition of polymeric precursor (DPP) previously reported [20,21]. Moreover, the present preparation method permitted to recover a high amount of material for large membrane-electrode-assembly (MEA) surfaces. Five hundred milligrams were obtained at once, which is 5 times more than the DPP method.

2. Experimental

All chemical reagents were of analytical grade and used without further purification. Ruthenium (III) chloride hydrate (RuCl₃·xH₂O, 99.99% metal basis) was purchased from Alfa Aesar. Ethanol absolute (CH₃CH₂OH > 99.8%) and Nafion solution (5 wt% in aliphatic alcohol) were obtained from Sigma Aldrich and ammonia solution (32% pure solution in water) was purchased from VWR.

2.1. Metal oxide synthesis and ink preparations

Ruthenium oxide electrocatalysts were synthesized using hydrolysis in ethanol medium. A 0.025 mol L⁻¹ ethanol solution containing the chloride precursors was prepared. This solution was homogenized in an ultrasonic bath for two hours. Pure ammonia was then added dropwise to the metallic solution under vigorous stirring leading to the instantaneous formation of a dark suspension of metal hydroxides. The pH was maintained at 12 during two hours with pure ammonia, in order to have a complete reaction. The particles were too small to be immediately separated by filtration. After five days, the solution has decanted and the resulting precipitate was collected to be then heated at 60 °C for removing the remaining traces of the solvent. After drying, the recovered material was submitted to a thermal treatment in air from room temperature to a temperature in the range 250 - 400 °C at heating rate 2 °C min⁻¹. The temperature was held for 1 h at 250, 350 and 400 °C to obtain small particle sizes of material free from organic carbon.

In order to compare the results presented herein with those previously obtained [20], the same ink composition was used. For each material, the catalytic powder (4 mg) was dispersed in a solution containing ultrapure water (725 μL) and Nafion® solution (114 μL). The ink was homogenized with an ultrasonic homogenizer during 10 minutes prior to each experiment.

2.2. Membrane electrode assembly preparation

The membrane electrode assembly (MEA) was prepared by the decal method, using commercial Pt/C catalyst (TEC10V50E, 46.1 wt%, Tanaka) at the cathode and the synthesized ruthenium oxide powder at the anode [21]. No carbon substrate was added to the anode catalyst to avoid its oxidation at high operating anode potentials in PEMWE. The ink was composed of the synthesized oxide and 10 wt.% Nafion® from a dispersion in aliphatic alcohol (D-520, 5 wt.%, DuPont) in an isopropanol solution and was sprayed on a PTFE circular substrate of 25 cm². The oxide loading was 1.2 ± 0.1 mg cm⁻². Conversely to the anode, the platinum particles (cathode catalyst) can be dispersed on a supporting substrate, since the hydrogen evolution reaction (HER) occurs with low overpotential. The ink contains the Pt/C catalyst (from Tanaka) and 27 wt.% Nafion® (D-520, 5 wt.%, DuPont) in deionized water. The cathode electrode was prepared by roll coating a Pt/C ink on a PTFE

substrate. The platinum loading was of 0.18 mg cm⁻². The two electrodes were transferred on a pretreated Nafion® 117 membrane (178 μm) by hot pressing at 135 °C and a pressure of 4 MPa. The MEA was then deposited in a single cell electrolyzer with a geometric surface area of 25 cm². A titanium sintered disc of 1.2 mm thick and a carbon gas diffusion layer (thickness of 350 μm) were used as current collectors for the anodic and cathodic sides, respectively. Titanium plates with diffusion channels were used as bipolar plates. Performances of the PEMWE cell were determined at 60 and 80 °C under atmospheric pressure.

2.3. Physical and physicochemical characterizations

The catalytic powders were characterized by different physical methods. The specific surface area of the material was evaluated using the Brunauer-Emmett-Teller (BET) theory. The sample was first outgassed at 573 K for at least 4 h under vacuum. The nitrogen adsorption isotherms were then measured at 77 K with an ASAP 2000 instrument (Micromeritics), using nitrogen (99.99% purity, Air Liquide).

The crystal structure of the material was determined by X-Ray Diffraction (XRD) measurements with an Empyrean diffractometer of PANalytical. This apparatus is equipped with a monochromatic copper tube ($\lambda_{\text{Cu-K}\alpha} = 0.154 \text{ nm}$) powered at 45 kV and 40 mA and an Xcelerator detector. The measurement was performed in scanning mode between 20 and 140° with a step of 0.05° and an accumulation time of 720 seconds per step. The powder sample was deposited on a silicon wafer after crushing and sifting.

The surface morphology of the materials was examined by transmission electron microscopy (TEM). TEM images were acquired with a JEOL 2100UHR (200 kV) electron microscope equipped with LaB₆ filament. The TEM grids were prepared by placing one drop of the particle solution on a copper grid and by evaporating the solution in the open atmosphere. X-ray fluorescence analysis also allowed estimating the material composition.

2.4. Electrochemical measurements

The electrochemical measurements (voltammetry, steady state polarization, chronopotentiometry and electrochemical impedance spectroscopy (EIS)) were performed in a three-electrode cell. A home-made reversible hydrogen electrode (RHE) prepared with the electrolyte solution and a glassy carbon slab were used respectively, as reference and counter electrodes. The RHE reference was connected to the cell with a Luggin capillary and referred all the potentials. The solution of 0.5 mol L⁻¹ H₂SO₄ (Merck, Suprapur) used as electrolyte was prepared with ultrapure water produced and purified with Millipore-Milli-Q system (18.2 MΩ cm at 20 °C). A gold slab of 0.55 cm² geometric surface was used as working electrode substrate. A cyclic voltammogram of this gold substrate was recorded in the supporting electrolyte prior to each measurement in order to verify the cleanliness of the cell. For each electrochemical experiment, the anode was prepared with 42 μL of catalytic ink deposited onto the gold substrate which corresponds to 0.38 mg cm⁻² of catalyst. The ink was dried under a low nitrogen flow at ambient temperature (U quality, supplied by Air Liquide). All the measurements were performed using an Autolab potentiostat/galvanostat (PGSTAT302) equipped with Nova 3.8 Software®. The EIS measurements were performed at different potentials. Fifty frequencies between 50 kHz and 10 mHz were scanned with an amplitude of 10 mV. Zview Software® was used to fit the EIS data with representative equivalent electrical circuit (EEC). The MEAs performances were measured in a 25 cm² single PEMWE cell at 60 and 80 °C and atmospheric pressure with a teststand which also permits the measurement of hydrogen

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