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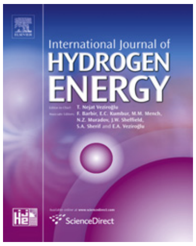

# Nanosized Pt/$IrO_2$ electrocatalyst prepared by modified polyol method for application as dual function oxygen electrode in unitized regenerative fuel cells

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ABSTRACT

A new generation of highly efficient and non-polluting energy conversion and storage systems is vital to meeting the challenges of global warming and the finite reality of fossil fuels. In this work, nanosized Pt/$IrO_2$ electrocatalysts are synthesized and investigated for the oxygen evolution and reduction reactions in unitized regenerative fuel cells (URFCs). The catalysts are prepared by decorating Pt nanoparticles (2–10 nm) onto the surface of a nanophase $IrO_2$ (7 nm) support using an ultrasonic polyol method. The synthesis procedure allows deposition of metallic Pt nanoparticles on Ir-oxide without causing any occurrence of metallic Ir. The latter is significantly less active for oxygen evolution than the corresponding oxide. This process represents an important progress with respect to the state of the art in this field being the oxygen electrocatalyst generally obtained by mechanical mixing of Pt and $IrO_2$. The nanosized Pt/$IrO_2$ (50:50 wt.%) is sprayed onto a Nafion 115 membrane and used as dual function oxygen electrode, whereas 30 wt.% Pt/C is used as dual function hydrogen electrode in the URFC. Electrochemical activity of the membrane-electrode assembly (MEA) is investigated in a single cell at room temperature and atmospheric pressure both under electrolysis and fuel cell mode to assess the perspectives of the URFC to operate as energy storage device in conjunction with renewable power sources.

## 1. Introduction

Hydrogen energy storage systems coupled to renewable power sources are being proposed as a means to increase energy independence, improve domestic economies, and reduce greenhouse gas emissions from stationary and mobile fossil-fueled sources [1–3]. New technologies for production and utilization of hydrogen as energy carrier include electrolysers [4–6] and fuel cells [7–9], respectively. Both processes may alternatively occur in the same device based on a proton exchange membrane (PEM). This device is called unitized regenerative fuel cell (URFC). Compared with conventional

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secondary batteries, URFCs advantages rely on high energy density, long-term energy storage, durability and environmental protection [10–13]. Whereas in comparison to the separate fuel cell and electrolyzer based systems, URFCs are significantly more compact and they allow considerable system simplification. URFC devices are characterized by rapid start up, they can operate efficiently at low temperature without the need of cumbersome power consuming auxiliaries. Moreover, they can provide stable operation even in the presence of a large number of start up/shut down cycles.

Nevertheless, the design of an oxygen electrode for an electrolyser is different than that of a fuel cell [14]. Carbon supported Pt electrocatalysts, currently used in fuel cells, are characterized by low catalytic activity and poor stability for oxygen evolution [15]. It is important to consider that the present Pt/C catalysts do not yet satisfy completely the stability requirements of a fuel cell cathode characterized by an operating potential window of 0.6–1.0 V vs RHE [16], whereas that of an oxygen evolution electrode, in an electrolyzer, is normally 1.5–2.0 V vs RHE [17,18]. Moreover, for the oxygen electrode in a polymer electrolyte fuel cell, the gas diffusion layer (GDL) is usually a highly hydrophobized carbon paper or carbon cloth [16]. However, this type of GDL cannot be used in an URFC mainly for the following two reasons: (i) the carbon material easily oxidizes to $CO_2$ at high potentials during water electrolysis causing poor stability, and (ii) GDLs must be characterized by an appropriate balance between hydrophobic and hydrophilic properties for both fuel cell and water electrolysis operation modes to promote mass transport of the reaction species to the catalytic sites and removal of reaction products [17]. While the electrode for a water electrolyser is generally designed to be flooded or partially flooded [17], the fuel cell operating at low temperatures must repel water to avoid electrode flooding thus allowing access of molecular $H_2$ and $O_2$ to the catalytic sites [16]. From such an analysis, it is clear that the URFC is not the simple linear combination of electrodes used in fuel cells with those used in electrolysis cells.

Beside these aspects, one of the main technical breakthroughs for URFCs is the development of efficient dual function electrocatalysts for the oxygen reaction [19–25]. Nanostructured electrocatalysts are attracting a deal of interest in this field since they have a strong impact on the dispersion of precious metals and the possibility of tailoring electrochemical properties due to the relevant influence of the surface characteristics on the overall behavior [1,26]. The materials for dual function oxygen electrodes actually include Pt–Ir [27,28], Pt-Ru-Ir [29], Pt-$IrO_2$ [30–34], Pt-$IrO_2$-$RuO_2$ [21,35]. Various methods have been used to prepare the separate catalytic $IrO_2$ and Pt phases forming the dual function electrocatalyst, i.e. Adams fusion, sol–gel, etc [36–38]. However, the final step is characterized in most cases by a mechanical grinding and mixing of the catalyst powders to form the dual function electrode [21]. It is considered that even extensive ball milling procedures can hardly allow to achieve a good mixing at an atomic level of the two phases to provide a suitable catalytic dispersion. Alternatively, the direct (one step) chemical synthesis of dual function catalyst is not a simple task. One critical aspect is regarding the achievement of nanosized metallic platinum nanoparticles in combination with a dispersed Ir-oxide phase. The occurrence of metallic Ir or a substoichiometric Ir-oxide phase during the Pt precursor reduction step to form Pt° may cause a decrease of electrocatalytic activity for water electrolysis [21,39]. The polyol process has recently received attention for preparation of fuel cell catalysts [40,41] because it provides a satisfactory control of Pt particle size and distribution without using any additional stabilizer [42–45]. By using ethylene glycol in the polyol process, metal ions are reduced to form a metal colloid; they receive electrons from the oxidation of ethylene glycol to glycolic acid, which is present in its deprotonated form as glycolate anions [46].

The novelty of the present approach consists in the use of modified polyol process to form Pt nanoparticles directly on a high surface area $IrO_2$ support by proper control of the reducing process. Formation of a metallic Pt on $IrO_2$ thus occurs without significant modification of the oxidation state of Ir. Accordingly, $IrO_2$-nanophase supported Pt nanoparticles were prepared by using an ultrasonic polyol method in order to obtain an efficient dual function catalyst for oxygen reduction (Pt) [45,47] and evolution ($IrO_2$) [48–50]. Characterization of catalysts was carried out by X-ray diffraction (XRD), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). It was studied the effect of Pt nanoparticles growth as a function of the pH of reaction and the reaction yield. The URFC processes were studied at room temperature and atmospheric pressure to assess their perspectives to operate as energy storage devices in combination with renewable power sources.

## 2. Experimental

### 2.1. *Preparation of Pt/$IrO_2$ electrocatalysts*

$IrO_2$ nanoparticles were prepared by using a low temperature colloidal method [50]. In order to obtain a dual function catalyst consisting of Pt supported on $IrO_2$ nanoparticles, the ultrasonic polyol method, commonly used to prepare Pt or other elements in a metallic form on a carbon support [51–55], was employed. 25 mL of ethylene glycol (Aldrich 99%) were placed in a beaker; this was kept in an ultrasonic bath for 10 min at ~70 °C. Afterwards, 50 mg of in-house prepared $IrO_2$ were added in the beaker and this solution was maintained under ultrasounds (frequency 40 kHz) at 70 °C for 10 min. Then, 1 mL of 0.5 M $H_2PtCl_6$ (22.75 wt.% of Pt, Engelhard) was added and reaction time was varied, with periods of 10, 30 and 60 min. The final solution was centrifuged for 30 min and filtered to separate liquid and solid phases. During the polyol synthesis process, the pH of the solution was varied in order to modulate the reducing power of ethylene glycol and thus the reaction rate. The effect of this parameter in determining the crystallite size of Pt was investigated. A scheme of the Pt-$IrO_2$ electrocatalyst preparation procedure is reported in Fig. 1.

### 2.2. *Physico-chemical characterization*

X-ray diffraction powder (XRD) patterns for these catalysts were obtained on a Philips X'Pert X-ray diffractometer using Cu Kα-source operating at 40 kV and 30 mA. The diffraction