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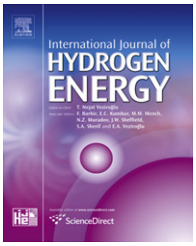

Preparation and study of IrO_2/SiC–Si supported anode catalyst for high temperature PEM steam electrolysers

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ABSTRACT

A novel catalyst material for oxygen evolution electrodes was prepared and characterised by different techniques. IrO_2 supported on a SiC–Si composite was synthesised by the Adams fusion method. XRD and nitrogen adsorption experiments showed an influence of the support on the surface properties of the IrO_2 particles, affecting the IrO_2 particle size. The prepared catalysts were electrochemically characterised by cyclic voltammetry experiments at 25,80,120 and 150 °C. In accordance with the observed variation in particle size, a support loading of up to 20% improved the activity of the catalyst. Powder conductivity measurements were also performed, which showed the influence of the support particles in the packing of IrO_2 particles, perhaps favouring the formation of channels and pores between particles, thus increasing the catalyst utilisation.

1. Introduction

Some of the future aspirations of the “hydrogen energy cycle” involve the splitting of water by means of electrolysis and using the evolved hydrogen as a fuel. One way to do this would be by using a proton exchange membrane (PEM) electrolyser [1]. The electrolysis of steam instead of liquid water is favourable in several ways. The thermodynamic demands are lower at higher temperatures, waste heat can be utilised (effective cooling due to temperature gradient) and water management is simplified in such systems (avoiding two-phase operation).

Elevated working temperatures involve increased demands for corrosion resistance of catalysts and construction materials (bipolar plates and current collectors), while the contact resistance in gas diffusion layer (GDL) should remain reasonable.

For conventional PEM water electrolysers, Nafion® is commonly used as an electrolyte [2–4]. The conductivity of such membranes decreases significantly at temperatures above 80 °C, which is associated with the reduction of water content [5]. Sufficient efficiency is achieved using polybenzimidazole (PBI) membranes doped with phosphoric acid in PEM fuel cells at temperatures up to 200 °C under ambient pressure [5,6]. Doped membranes are a potential electrolyte for use in PEM steam electrolyser systems. Nevertheless, one of the main problems in such systems still remains the extremely low pH combined with elevated temperatures and high overpotentials at the anodic compartment. These conditions impose serious limitations on the materials which can be used.

The applicable electrocatalysts for the oxygen evolution reaction (OER) are still limited to Ir, Ru and their oxides [7]. The anodes used in research and in industry are mostly based on mixtures of an electrocatalyst and a stabilising agent, e.g.

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TiO_2. Such kinds of electrodes are known as dimensionally stable anodes (DSA) and were first developed by Beer [8–10].

For Nafion® based systems, porous *Ti* usually serves as an anode bipolar plate and GDL material [4,11]. Unfortunately, previous studies have shown that titanium can not be used in systems that involve phosphoric acid containing electrolytes [12,13].

Ruthenium oxide is known as the most active catalyst for the OER. Nevertheless, according to thermodynamical calculations, the oxidation of RuO_2 to RuO_4 occurs at potentials more positive than 1.387 V (vs. SHE) [14]. The instability of Ru-based anodes at high overpotentials in acidic conditions has been proved by several studies. The mechanism of corrosion is explained by the conversion of RuO_2 to soluble, non-conductive and volatile RuO_4, with a boiling point of 130 °C [15–17]. The facts mentioned above present *Ru* and its oxides as unsuitable catalysts for the OER in high temperature PEM steam electrolysers.

Several studies undertaken [18,19] devoted to improving the stability of RuO_2 during anodic oxygen evolution by mixing the catalyst with IrO_2. This causes a decrease in the corrosion rate of RuO_2 dependant on the IrO_2 content in the mixture. IrO_2 appears to have greater stability and a reasonable activity compared with Ru-based electrocatalysts for such systems [7]. Apparently, IrO_2 is the most stable OER electrocatalyst for PEM water electrolysers studied until now.

Unfortunately, high loadings of noble metals or their oxides puts considerable commercial limitations on a wider application of PEM electrolysers and a significant reduction of such metal loadings should be achieved [20]. In search for an electrode with lower loading requirement for the electrocatalyst, two main strategies can be followed:

The first includes doping of active oxides with other, more available materials, such as SnO_2, SbO_2, TaO_2, Mo_xO_y etc [1,21–23]. This approach involves introduction of a dopant precursor on the initial stage of catalyst synthesis. Following this method, composite binary or ternary catalytic oxides are usually obtained.

The second approach includes the use of a support material which would improve the specific surface area of the electrocatalyst and prevent particle agglomeration, thus increasing the specific surface area of the electrode.

Ideally, raw materials for the preparation of inert anode or/and its support should be cheap and readily available.

Carbon is a widely used catalyst support material for PBI fuel cells. On the other hand, one of the main reasons for fuel cell catalyst degradation is the corrosion of the carbon support, which occurs at potentials higher than 0.207 V (vs. SHE) [5,24]. In electrolysis mode the corrosion speed of carbon would be much higher than in fuel cell mode due to the higher anodic overpotentials of the OER. For this reason, carbon cannot be considered as a potential durable support for anode electrocatalyst in PEM electrolysers. The corrosion stability and durability of the OER electrocatalyst support appears to be one of the greatest challenges in the field.

In conclusion, only a dimensionally and chemically stable, as well as readily available and reasonably conductive material should be used for this application. Among others, ceramic materials are potentially promising candidates [25]. However, most ceramics have relatively low electrical conductivity while it is considered to be of high importance for the overall performance of electrodes. The value of the acceptable electrical conductivity of catalytic layers is discussed elsewhere [26].

Nevertheless, some of the materials with low electrical conductivity can be used as an anode for acidic systems [27]. In one study in particular, p–Si was employed as a substrate for thermal deposition of the active IrO_2 and results showed that this material can be used for the preparation of DSA-type electrodes.

Silicon carbide, produced by the Acheson process is known as a hard, refractory and chemically inert material [28]. Electrical conductivity of this material is quite poor, however doping with appropriate elements can significantly increase this property [29]. Considering a possible electrochemical application of silicon carbide, the main advantage among others is its high stability in phosphoric acid solutions [30].

Several studies have been published, reporting the successful use of silicon carbide as a catalyst support for PEM fuel cells [31,32]. However, at present there are almost no publications covering catalyst support investigations for electrolysers [33]. Indeed, this area of research is more challenging and the material choice is highly limited, which is directly connected with the increased cell voltages applied in the electrolyser mode.

In this study a refractory silicon carbide-silicon material (free *Si* less than 22%) was used as a support for the active OER catalyst IrO_2. The aim being to find a stable support and introduce it to the active catalyst.

2. Experimental part

2.1. *SiC–Si/IrO$_2$ powder catalyst preparation*

The sintered SiC–Si material was provided by the “State Powder Metallurgy Plant”, Brovary, Ukraine. Catalyst support powder was prepared according to the following procedure: the as-received plate was cut with a diamond saw into squared samples with 1 *cm* side. The thickness of the plates was 2 mm. The prepared plates were cleaned in an ultrasonic bath, degreased with acetone, washed with demineralised water and finally dried at 80 °C. The silicon carbide-silicon plates were milled in a planetary ball mill (Fritsch, Pulverisette 7). Since SiC is a material with high hardness, a mill made of conventional steels could not be used for this procedure. This is due to the relative softness of the steel, and associated risk of contamination of the sample by self abrasion of the steel balls and a possible tribochemical reaction. Therefore, two 45 ml steel vials, covered with tungsten carbide wear resistant lining were used. Milling was performed in the vial, which contained 6 WC balls, each 15 mm in diameter. The working vial contained 2 g of the starting material. The mill was operated at 730 r.p.m. for 10 min.

The product of the milling was introduced at the initial stage of the Adams fusion method of IrO_2 synthesis [34]. The iridium oxide content in the prepared catalyst was varied from 0 to 100 wt.% in steps of 10 wt.%. As the support was added to the initial solution of the catalyst precursor, it was expected that the catalyst would adhere to the surface of the