



Metal Carbide and Oxide Supports for Iridium-Based Oxygen Evolution Reaction Electrocatalysts for Polymer-Electrolyte-Membrane Water Electrolysis



Fatemeh Karimi, Brant A. Peppley*

Department of Chemical Engineering, Queen's University, 19 Division St., Kingston, Ontario, K7L 3N6, Canada

ARTICLE INFO

Article history:

Received 22 January 2017

Received in revised form 6 June 2017

Accepted 7 June 2017

Available online 15 June 2017

Keywords:

Oxygen Evolution Reaction

PEM Water Electrolysis

Metal Carbide and Oxide Support

Polyol Synthesis

Iridium Electrocatalyst

ABSTRACT

Iridium based materials are one of the most active electrocatalysts used for the oxygen evolution reaction (OER) in polymer electrolyte membrane (PEM) water electrolyzers. To increase the utilization, the iridium electrocatalyst is typically dispersed on a high-surface area support material. This results in less iridium being required and consequently reduced catalyst cost. In this work, six metal carbides and oxides were characterized and evaluated as supports for iridium electrocatalyst. The supports studied included: tantalum carbide (TaC), niobium carbide (NbC), titanium carbide (TiC), tungsten carbide (WC), niobium oxide (NbO₂), and antimony-doped tin oxide (Sb₂O₅-SnO₂).

© 2017 Elsevier Ltd. All rights reserved.

The thermal stability, electrical conductivity, specific surface area, and electrocatalytic activity of these support materials were measured before the iridium electrocatalyst was dispersed on the surface.

Afterwards, 20 wt% iridium was dispersed on each of the supports using the polyol method, and the resultant BET surface area, electrical conductivity and OER activity of the synthesized supported catalysts were compared with the support material alone. The two most promising supports, TaC and NbO₂, were ball-milled for durations varying between 1 to 7 days to reduce the particle size and increase the surface area. As before, 20 wt% supported iridium electrocatalysts were synthesized. Increase in the surface area of TaC increased the mass-specific OER performance by 75%, but no significant change in the performance was observed for NbO₂. For both TaC and NbO₂, increase in the surface area decreased the powder electrical conductivity of the supported catalysts.

A series of catalysts was then prepared to study iridium loading (2, 5, 10, 20, 30 and 100 wt% Ir). BET surface area, electrical conductivity, and OER activity were measured for each catalyst loading and also for the unsupported catalyst. The mass specific

OER activity showed a clear maximum around 5 wt% iridium loading.

1. Introduction

The increasing world energy need, the depletion of fossil fuels, and concerns about greenhouse gases emissions demand development of a new energy vector, and hydrogen as an energy carrier has been widely mentioned as a solution to world energy problems [1–3]. Polymer electrolyte membrane water electrolysis (PEMWE), where electricity splits the water to high purity oxygen and hydrogen, is a beneficial method to produce hydrogen from renewable energy sources like wind, solar and hydro. However, the widespread commercialization of PEMWE is limited due to problems associated with the substantial overpotential losses and durability issues of oxygen evolution reaction (OER) electrocatalyst in anode [4–6]. The most active material with the lowest overpotential for OER are iridium and ruthenium based electrocatalysts [7–9]. However, ruthenium has been shown to be unstable [10,11] in the acidic OER environment. Iridium has been shown to be more stable [9] and thus has been used exclusively as OER electrocatalyst [5,12–17]. Due to the high cost of iridium material different approaches are taken to increase the utilization of iridium electrocatalyst.

One approach is doping the iridium electrocatalyst with some inexpensive metals, which can improve the performance and

* Corresponding author.

E-mail address: brant.peppley@queensu.ca (B.A. Peppley).

stability of iridium due to changes in the electronic and structural properties. Some of these doping elements include tantalum [18–20], tin [4,21,22], tin and tantalum [23], tin and antimony [24,25], molybdenum [26], and manganese [27]. The resulting electrocatalyst usually is a binary or ternary composite of iridium oxide with the other metal oxides in the form of $\text{Ir}_x\text{M}_y\text{N}_z\text{O}_a$, M and N being the inexpensive metals. This approach is often used to make Dimensionally Stable Anodes (DSA), where a layer of OER electrocatalyst is deposited on a substrate (usually titanium), rather than coating it on a membrane to make Membrane Electrode Assemblies (MEAs).

Another approach is to use a high-surface area support for the electrocatalyst [14,28]. Using a support reduces the agglomeration of the electrocatalyst and increases the active surface area. When the supported catalyst is coated on the electrolyte membrane, larger supported particles penetrate less through the layers and stay in contact with the polymer electrolyte membranes [5]. As a result, a lower rate of electrocatalyst loss and a higher efficiency of electrocatalyst utilization is achieved. There are several requirements for a suitable support for OER electrocatalyst: 1) high availability and low cost; 2) high stability in the acidic OER environment; 3) high specific surface area; and 4) good electrical conductivity. Polonsky et al. [28]; however, have reported that the conductivity of a support is not critical and non-conductive materials might also be considered as support for IrO_2 catalyst. This is because the conductivity of IrO_2 alone is enough for the operation of PEMWE and a sufficient loading of IrO_2 provides acceptable electrical conductivity. In addition to the above-mentioned requirements for a support it is desirable that the support itself has some electrocatalytic activity, and preferably improves the electrochemical activity and durability of the electrocatalyst through influencing its electronic structure [29,30]. Various materials have been used as support for iridium for the OER in PEMWE such as: TiO_2 [5], titanium suboxide ($\text{Ti}_n\text{O}_{2n-1}$) [13], SnO_2 [12,31], Antimony-doped SnO_2 [32–36], TiC [37], SiC-Si [14], and TaC [28,38].

The major disadvantage of metal oxides supports such as SnO_2 and TiO_2 is their low electrical conductivity. Mazur et al. [5] reported that due to the low electrical conductivity of TiO_2 a high loading of iridium electrocatalyst is required to have a sufficient conductivity for the supported catalyst in PEMWE. Adamaki et al. [39] have shown that Magneli phase $\text{Ti}_n\text{O}_{2n-1}$ has significantly higher conductivity compared to TiO_2 . Siracusano et al. [13] have developed a procedure to synthesize titanium suboxides ($\text{Ti}_n\text{O}_{2n-1}$) with Magneli phase, which were successfully used as a support for iridium oxide. In the case of SnO_2 , doping it with antimony (Sb) is a common approach to increase its electrical conductivity [40,41]. Antimony-doped tin oxide (ATO) has been used in many research studies as a promising support for OER electrocatalysts [32–36,42]. ATO with high surface area has been synthesized by a colloidal method [36] or a hydrothermal method [47], and it has been reported that it can potentially improve the stability of iridium and ruthenium electrocatalyst in a supported catalyst [32,43]. However, doping tin oxide with antimony might also increase the corrosion rate in the acidic environment [44]. Antimony oxide has poor stability itself [45]. Overtime the improved conductivity caused by Sb_2O_5 could decrease resulting in increasing Ohmic losses in the catalyst layer. It has been reported that doping the ATO with Pt could increase its stability [46]; however, this is not a desirable option as Pt doping would significantly increase the cost of the catalyst.

Transition metal carbides have attracted much attention recently as potential support materials [47,48] or as electrocatalysts [49–51]. Many transition metal carbides show good electrical conductivity, high chemical stability, good electrocatalytic activity, and excellent mechanical stability [48,51]. Some transition metal carbides such as

TiC [37], SiC-Si [14], and TaC [28,38] have been used as supports for iridium oxide for the OER in PEMWE.

Nikiforov et al. [14] and Polonsky et al. [28,38] have used the high temperature Adams fusion method [52] to synthesize supported IrO_2 using SiC-Si and TaC as support, respectively. In this method iridium nitrate, obtained from the interaction between an iridium precursor salt (H_2IrCl_6) and NaNO_3 , is heated to temperatures greater than 500°C and a IrO_2 with a crystalline rutile structure is synthesized. The high temperatures used in the Adams fusion method can be tolerated by a limited number of materials without being thermally oxidized. Polonsky et al. [28] have reported that during the synthesis of IrO_2/TaC catalyst by the Adams fusion method, a low conductivity surface film of NaTaO_3 was formed due to oxidation of TaC by NaNO_3 at high temperatures (around 500°C). Ma et al. [37] have also used a chemical reduction technique to synthesize iridium catalyst with a crystalline structure supported on TiC. It has been repeatedly stated that amorphous IrO_x has higher OER activity compared to crystalline IrO_2 [15,53,54]. Amorphous IrO_x could be synthesized with low temperature synthesis methods such as the polyol method. The polyol method [55] is a fast, simple, and low cost technique that enables synthesis of nanosize materials including IrO_x with amorphous structure and high OER activity for PEMWE [35,56,57]. However, the polyol method has not previously used to synthesize an OER electrocatalyst supported on transition metal carbides for PEMWE. In this work a number of metal carbides and metal oxides are examined for OER electrocatalyst support; The polyol method is used to synthesize the supported iridium catalysts; The measured OER performance is related to the properties of supports and the supported catalysts.

The result of this work is divided into four sections. In the first section: tantalum carbide (TaC), niobium carbide (NbC), titanium carbide (TiC), tungsten carbide (WC), niobium oxide (NbO_2), and antimony-doped tin oxide ($\text{Sb}_2\text{O}_5\text{-SnO}_2$), in the form as supplied by Sigma-Aldrich were characterized and compared as supports for OER electrocatalysts. For the second section, the polyol method was used to synthesize 20 wt% IrO_x catalyst on the supports. The specific surface area, electrical conductivity and OER activity of these supported catalysts were then compared. In the third section, the effect TaC and NbO_2 surface area on the performance and OER activity of the supported catalysts was studied. Finally, in the last section, the effect of iridium loading on the conductivity, surface area and OER activity of a TaC supported catalyst was examined.

2. Experimental

2.1. Chemicals

All the chemicals were purchased from Sigma-Aldrich[®], unless otherwise noted. Tantalum (IV) carbide (TaC, $\leq 5\ \mu\text{m}$, 99.99%), niobium (IV) carbide (NbC, $5\ \mu\text{m}$, 97%), niobium (IV) oxide (NbO_2 , $5\ \mu\text{m}$, 99.99%), titanium (IV) carbide (TiC, $< 200\ \text{nm}$, 99.99%), tungsten (IV) carbide (WC, $2\ \mu\text{m}$, $\geq 99\%$), and antimony-doped tin oxide ($\text{Sb}_2\text{O}_5\text{-SnO}_2$, $< 50\ \text{nm}$, $\geq 99.5\%$) were used as support for iridium catalyst. To synthesize iridium based electrocatalyst with the polyol method, the iridium (III) chloride hydrate ($\text{IrCl}_3\cdot x\text{H}_2\text{O}$) was used as metal precursor; ethylene glycol (anhydrous, 99.8%) was used as solvent and reducing agent; and sodium hydroxide (NaOH, ACS reagent) and sulfuric acid (H_2SO_4 , 95–98%, Fisher Scientific) were used for adjusting pH during the synthesis process.

2.2. Ball milling

TaC and NbO_2 were ball milled using zirconia ceramic balls (5 mm diameter) in a polyethylene vial containing approximately

Download English Version:

<https://daneshyari.com/en/article/6470570>

Download Persian Version:

<https://daneshyari.com/article/6470570>

[Daneshyari.com](https://daneshyari.com)