



Short communication

Comparative study of oxygen reduction reaction on $\text{Ru}_x\text{M}_y\text{Se}_z$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) electrocatalysts for polymer exchange membrane fuel cellK. Suárez-Alcántara^a, O. Solorza-Feria^{b,*}^a Depto. Ciencia de Materiales, ESFM-IPN, UP-ALM, Zacatenco, G.A. Madero, C.P. 07738, México, D.F., Mexico^b Depto. Química, Centro de Investigación y de Estudios Avanzados del IPN, A. Postal 14-740, 07360 México, D.F., Mexico

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ABSTRACT

Electrochemical evaluation of the $\text{Ru}_x\text{M}_y\text{Se}_z$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) type electrocatalysts towards the oxygen reduction reaction (ORR) is presented. The electrocatalysts were synthesized by reacting the corresponding transition metal carbonyl compounds and elemental selenium in 1,6-hexanediol under refluxing conditions for 3 h. The powder electrocatalysts were characterized by scanning electron microscopy (SEM), and X-ray diffraction (XRD). Results indicate the formation of agglomerates of crystalline particles with nanometric size embedded in an amorphous phase. The particle size decreased according to the following trend: $\text{Ru}_x\text{Cr}_y\text{Se}_z > \text{Ru}_x\text{W}_y\text{Se}_z > \text{Ru}_x\text{Mo}_y\text{Se}_z$. Electrochemical studies were performed by rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques. Kinetic parameters exhibited Tafel slopes of 120 mV dec^{-1} ; exchange current density of around $1 \times 10^{-5} \text{ mA cm}^{-2}$ and apparent activation energies between 40 and 55 kJ mol^{-1} . A four-electron reduction was found in all three cases. The catalytic activity towards the ORR decreases according to the following trend: $\text{Ru}_x\text{Mo}_y\text{Se}_z > \text{Ru}_x\text{W}_y\text{Se}_z > \text{Ru}_x\text{Cr}_y\text{Se}_z$. However this trend was not maintained when the materials were tested as cathode electrodes in a single polymer exchange membrane fuel cell, PEMFC. The $\text{Ru}_x\text{W}_y\text{Se}_z$ electrocatalyst showed poor activity compared to $\text{Ru}_x\text{Mo}_y\text{Se}_z$ and $\text{Ru}_x\text{Cr}_y\text{Se}_z$ which were considered suitable candidates to be used as cathode in PEMFCs.

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1. Introduction

Worldwide interest in clean energy generation systems such as fuel cells technology has motivated research on the synthesis, characterization and evaluation of novel and stable oxygen reduction electrocatalysts for the direct four-electron transfer process to water formation [1–3]. The oxygen reduction reaction (ORR) in acid media has been investigated extensively due to its importance in many energy device applications [4]. The commercial application of this technology relies on the development of an effective electrocatalyst to overcome the inherent slow kinetics and high electrode overpotentials of current ORR electrocatalysts. Several approaches have been explored but essentially the best results are obtained with the use of platinum, platinum-based or noble metal-based nanostructured materials [5,6]. This kind of materials presents adequate activity towards ORR but in addition, the suitable materials should be able to show appropriate long-term stability. Another important factor to be considered in the design of ORR electrocatalysts is the specific application and market. In this field we have reported that Ru-based electrocat-

alysts in the nanometric size range exhibited attractive kinetic properties as cathode electrodes for polymer exchange membrane fuel cells, PEMFC [7,8]. The present research reported herein is aimed to synthesize, characterize and evaluate Ru-based electrocatalysts for their potential application in PEMFC. Specifically, this paper compares the kinetic performance of bimetallic chalcogenides of the type $\text{Ru}_x\text{M}_y\text{Se}_z$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) as ORR cathode electrocatalyst for PEMFC. If successful, these materials can be an alternative to the Pt-cathode electrocatalyst and with potential applications in non-extensive power-demanding fuel cells. The amount of the noble metal (Ru) can be reduced and the activity towards the ORR improved, compared to a pure noble metal electrocatalyst.

Extensive studies has been reported showing that Ru-based materials present catalytic activity towards ORR, but with the incorporation of Se as a second transition metal the activity and selectivity improves significantly [9,10]. The second transition metal was selected by their capability to form compounds having several oxidation states. In this context, the aim of the present study is to compare in terms of ORR kinetics and fuel cell performance, the incorporation of a second metal, within the ruthenium–selenium matrix and to show how a synergistic effect can improve the stability and enhance the catalytic activity of bimetallic chalcogenides.

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