Electrochimica Acta 89 (2013) 106–113

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Oxide loading effect on the electrochemical performance of $LaNiO_3$ coatings in alkaline media

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ARTICLE INFO

Article history:
Received 22 July 2012
Received in revised form
13 November 2012
Accepted 14 November 2012
Available online xxx

Keywords:
$LaNiO_3$ films
Nickel-foam support
Roughness
Cyclic voltammetry
Electrochemical impedance spectroscopy

ABSTRACT

$LaNiO_3$ film electrodes were prepared by brush painting using nickel-foam supports in order to increase its surface area available for electrochemical reactions. Loadings varying between 20 and 140 mg cm^{-2} were tested. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate the coatings roughness (R_f) and morphology (φ) factors, complemented by optical microscopy observations. The values obtained from the two methods are in excellent agreement. The R_f values, ranging from 848 ± 50 to 4260 ± 60, are within the highest in the open literature.

A simulation, of the effect of the oxide loading on the coatings R_f values, was performed using just the experimental values of the roughness factors for oxide free foam and pelleted electrodes. It was found that the increase of oxide loading causes a quasi linear increase of the electrodes active surface area. Simulated values were in excellent agreement with the experimental roughness factors and pore resistances obtained by CV and EIS. The electrodes were tested for oxygen evolution.

1. Introduction

$LaNiO_3$ perovskite-type oxide is one of the most favorable candidates for oxygen evolution [1–6] and reduction in alkaline solutions [7] and is often been referred as a potential bifunctional oxygen electrode [8,9]. It is well established that oxide powder synthesis conditions as well as electrode fabrication are key factors to control the electrocatalytic activity of $LaNiO_3$ coatings [6,10,11]. In recent publications the use of Ni foam, as support, has been emphasized due to its unique characteristics namely low contact resistance between the oxide and support, possibility of high metal oxide loadings and dimensional stability [12,13].

In previous works, the authors reported the preparation of $LaNiO_3$ powder, by a self-combustion method, and used it to obtain oxide coatings on Ni foam supports [14,15]. The experimental method used to synthesize the oxide coupled with the use of Ni foam as support has proved to be very effective in producing oxide electrodes with surface areas higher than those referred in literature. The prepared electrodes showed very high surface area possibly associated with the oxide loading. However no systematic studies were performed, in order to establish a clear relationship between oxide loading and surface area.

Studies on the loading effect on metallic substrates were found in literature [10,11], however as the best of our knowledge no such studies on metallic foam substrates were published.

The main objective of this work is to investigate how the electrochemical active area of the $LaNiO_3$ coatings are affected by the oxide loading, having in mind the potential use of metallic foams as supports for oxide electrodes.

In addition we also pretend to improve the preparation conditions of $LaNiO_3$ coatings on Ni foam supports in order to increase its surface area available for the oxygen evolution reaction when compared with the best $LaNiO_3$ electrodes referred to in relevant literature [4 and references therein].

We focus our study on the dependence of the surface area expressed in terms of roughness (R_f) and morphology (φ) factors on the oxide loading. Loadings varying between 20 and 140 mg cm^{-2} were tested. The global aspect of the electrodes was observed by optical microscopy. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to evaluate R_f and φ values. The electrodes were tested for oxygen evolution.

2. Experimental

The perovskite-type oxide $LaNiO_3$ was prepared by a self-combustion method using citric acid as previously reported [14,15]. Stoichiometric amounts of La_2O_3 (99.95%, Sigma–Aldrich), previously heated at 1173 K and Ni (99.99%, Sigma–Aldrich) were

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0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2012.11.040