Oxide loading effect on the electrochemical performance of LaNiO₃ coatings in alkaline media

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Abstract

LaNiO₃ film electrodes were prepared by brush painting using nickel-foil 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 (Rₜ) and morphology (ϕ) factors, complemented by optical microscopy observations. The values obtained from the two methods are in excellent agreement. The Rₜ values, ranging from 848 ± 50 to 2660 ± 60, are within the highest in the open literature.

A simulation of the effect of the oxide loading on the coatings Rₜ values, was performed using just the experimental values of the roughness factors for oxide free foam and pelletized 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.

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1. Introduction

LaNiO₃ 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 LaNiO₃ 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 LaNiO₃ 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 electrocatalytic active area of the LaNiO₃ 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 LaNiO₃ coatings on Ni foam supports in order to increase its surface area available for the oxygen evolution reaction when compared with the best LaNiO₃ 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 (Rₜ) 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 Rₜ and ϕ values. The electrodes were tested for oxygen evolution.

2. Experimental

The perovskite-type oxide LaNiO₃ was prepared by a self-combustion method using citric acid as previously reported [14,15]. Stoichiometric amounts of La₂O₃ (99.95%, Sigma−Aldrich), previously heated at 1173 K and Ni (99.99%, Sigma−Aldrich) were