Journal of Power Sources 375 (2018) 310–319

Contents lists available at ScienceDirect

Journal of Power Sources

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

Electrochemical modification of nickel surfaces for efficient glycerol electrooxidation

Mohamed S.E. Houache [a], Emily Cossar [a], Spyridon Ntais [b], Elena A. Baranova [a, *]

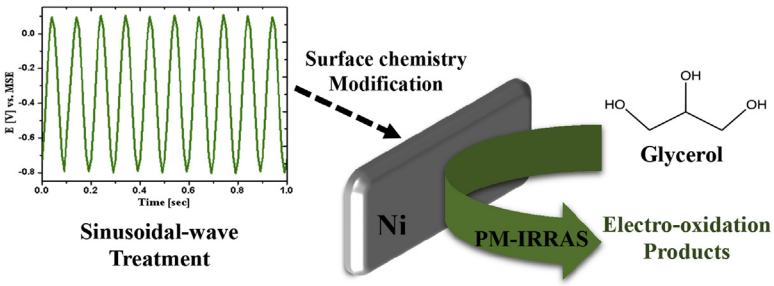
[a] Department of Chemical and Biological Engineering, Centre for Catalysis Research and Innovation (CCRI), University of Ottawa, 161 Louis-Pasteur, Ottawa, ON K1N 6N5, Canada

[b] Université de Lyon, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256, CNRS, Université Claude Bernard Lyon 1, 2 Avenue A. Einstein, 69626 Villeurbanne, France

HIGHLIGHTS

- Glycerol electrooxidation on untreated and pre-treated Ni surface.
- Electrochemical pretreatment of Ni in ascorbic acid using sin-wave profile.
- After treatment Ni surface consists mostly of hydroxides Ni^{2+} and Ni^{3+}.
- Pre-treatment significantly enhances Ni electrocatalytic activity.
- In-situ identification of reaction products with PM-IRRAS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 June 2017
Received in revised form
21 August 2017
Accepted 22 August 2017
Available online 6 September 2017

Keywords:
Glycerol electrooxidation
Nickel
Alkaline solution
Electrochemical treatment
PM-IRRAS

ABSTRACT

The Glycerol electrooxidation reaction (GEOR) was investigated on nickel electrode in alkaline media following a sinusoidal-wave treatment in a solution of 0.1 M Na_2SO_4 + 30 mM ascorbic acid. This treatment significantly increased the catalytic activity of Ni towards the GEOR. The electrochemical active surface area showed a six-fold increase, while the current density of glycerol oxidation was enhanced over nine times with a concurrent onset potential decrease by 45 mV. SEM analysis before and after the treatment revealed some morphology changes through the formation of additional grooves and pits on the Ni surface. XPS confirmed that before the treatment, the surface consists of Ni metal in addition to NiO, $Ni(OH)_2$ and NiOOH, whereas after the treatment, 97% of the surface is Ni hydroxide composed of Ni^{2+} and Ni^{3+}. Chronoamperommetry coupled with *in-situ* polarization modulation infrared-reflection absorption spectroscopy (PM-IRRAS) for simultaneous analysis of products on the Ni surface and in the bulk solution showed that the main reaction products on both untreated and treated Ni surfaces are glyceraldehyde, carbonyl, carboxylate ions and some carbon dioxide.

1. Introduction

Depletion of fossil fuel resources and their consumption is progressively increasing due to the growing global energy demand. In this milieu, there is a noteworthy need in developing more sustainable alternatives to petroleum-derived fuels to satisfy the global energy requirements [1,2]. Biodiesel, a clean-burning

* Corresponding author.
E-mail address: elena.baranova@uottawa.ca (E.A. Baranova).

http://dx.doi.org/10.1016/j.jpowsour.2017.08.089
0378-7753/

renewable biofuel is considered as an alternative fuel due to environmental, economic and technical sustainability. Biodiesel is derived from vegetable oils or animal and/or waste fats through a *trans*-esterification reaction. This process generates 10 wt% of glycerol as by-product [3]. Although glycerol is utilized as raw material in the pharmaceutical, food, cosmetics and tobacco industries, the glycerol supply is still superior to the demand due to the expansion of biodiesel production. The surplus of glycerol has motivated the research that transforms glycerol into value-added products thus, making biodiesel environmentally benign with added financial benefits [4].

Glycerol electrooxidation is an attractive approach for the synthesis of valuable chemicals. The electrochemical partial oxidation of glycerol in alkaline media consists of complex reaction pathways [5] and produces a large number of useful intermediates, such as glycerate, tartronate, oxalate, hydroxypyruvate, glycolate, dihydroxyacetone, mesoxalate and formate ions. A mixture of these products during the glycerol electrooxidation reaction (GEOR) has been observed and reported in literature [6–11]. Some of these oxygenated species have industrial uses, from heavy metal complexing agents to polymer precursors or drug delivery agents. For instance, tartronic acid is valued at 1564 USD/g and is utilized in medicinal practice [5]. Furthermore, glycerol electrooxidation in direct alcohol fuel cells (DAFCs) could potentially cogenerate electrical energy and produce a large number of high value-added chemicals [11–15]. This is in spite of its relatively low theoretical energy density of 5.0 $kWh.kg^{-1}$ if compared to ethanol and methanol, 8.1 and 6.1 $kWh.kg^{-1}$, respectively [16].

A number of recent studies showed the GEOR on noble metals such as Pt, Pd and Au [17–23], which had satisfactory activity but low selectivity towards the desired products. To make the GEOR practically valuable, novel inexpensive and selective catalysts are necessary. Ni is one of the most commonly used non-noble metal catalyst and has been applied in numerous electrochemical systems such as fuel cells [24], alkaline batteries [25], sensors [26], supercapacitors [27] and as electrocatalysts for alcohol oxidation reactions in alkaline media [4,28–32]. The complexity of the Ni surface chemistry in alkaline solutions and the Ni oxidation state does however strongly influences its efficiency, performance and catalytic activity [33–36]. Nevertheless the high activity of nickel, its anti-poison ability and long-term stability in alkaline solutions make it an attractive candidate for the GEOR. Several studies have reported a successful GEOR on Ni-based electrocatalysts [4,28,29] and on different bimetallic Ni-M/C (M = Co, Fe, Pd, Pt) nanoparticles [4,28,29,37–41]. In particular, the bimetallic Pt_2Ni_1/C catalyst showed a marked reaction rate increase due to modification of the electronic and geometric structure in comparison to the Pt/C catalyst. This results in better catalytic performance for glycerol electro-oxidation as shown by a lower onset potential and higher current densities [39]. The Ni co-catalyst was therefore able to reduce considerably the Pt amount without reducing the activity.

Due to the complexity of glycerol oxidation mechanism and the variety of the produced compounds, it is necessary to monitor, control and link, if possible, the different products to reaction conditions, applied potential and the surface species of an electrocatalysts. Coupling electrochemical methods, e.g., chronoamperometry (CA) and/or linear sweep voltammetry (LSV) with *in-situ* vibrational spectroscopy to identify products for alcohol oxidation has been successfully applied for monitoring GEOR products [19,42–44]. It was shown that Ni-based catalysts such as Ni/C, NiCo/C, NiCoFe/C and Pd_xNi_{1-x}/C in alkaline media produce various compounds, e.g. glycerate, glycolate, tartronate, oxalate and formate [14,15,28,29]. A scheme of glycerol oxidation on PdNi and PdAg in alkaline media was proposed earlier [14], in which the first step of the mechanism is glyceraldehyde formation, which is further oxidized to glycerate ion. The next step, depending on the nature of surface active sites and applied potential, could lead to formation of three intermediates: tartronate, formate and/or glycolate ions. The complexity of the reaction pathway implies that in order to design Ni-based electrocatalysts with bespoke activity and selectivity it is crucial to gain a better understanding of the nature of the Ni surface active sites and their role on GEOR and product distribution.

In the present study, we report the glycerol electrooxidation reaction on a polycrystalline Ni electrode. We investigate the reaction on untreated and electrochemically pre-treated Ni surfaces. The proposed treatment is based on the work of Baranova et al. [45], where an electrochemical sinusoidal-wave treatment was applied to Ni-based particles ($Ni_{99}Pd_1$) to improve their activity towards hydrogen evolution reaction (HER). The sinusoidal wave treatment in the presence of ascorbic acid resulted in a significant current density increase for HER due to the formation of a higher amount of Ni surface hydroxides. In the later study [46], the improved HER after square-wave treatment in the same electrolyte solution and potential window was associated with formation of surface $Ni(OH)_x$ (x between 0 and 2) that promoted the reaction. Therefore, in this work the Ni electrode before and after the sine-wave treatment was characterized by SEM and XPS to elucidate the role of treatment in the Ni morphology and surface chemistry. Furthermore, a detailed electrochemical study in combination with *in-situ* (PM-IRRAS) measurements was carried out to compare the activity of Ni before and after treatment and find the reaction products.

2. Experimental

2.1. Materials and electrochemistry

Electrochemical measurements were carried out using two conventional three-electrode electrochemical cells, namely, Teflon cell for the electrochemical oxidation of glycerol in alkaline solution and a cell made of Pyrex for electrochemical sinusoidal-wave treatment. BioLogic VSP Potentiostat/Galvanostat equipped with EC-Lab software (BioLogic Science Instruments SAS, Claix, France) was used to conduct all electrochemical measurements. The nickel wire (99.99% purity, Sigma Aldrich) of 0.5 mm in diameter served as a working electrode. Prior to each experiment, the "fresh" untreated Ni wire was polished using an aqueous suspension of 30 μm alumina (Al_2O_3, Carveth metallurgical limited, Canada) and 3 μm Al_2O_3 (Buehler, USA) to obtain a mirror-like surface. The Ni wire was then rinsed with de-ionized water (Milli-Q® Millipore, 18.2 MΩ cm at 293 K) and sonicated in an ultrasonic bath for 20 min. Once polished, the Ni wire was placed in a Teflon casing, leaving a 1 cm portion of the wire exposed to the solution. This resulted in a geometric area of 0.161 cm^2. Large surface area Pt mesh was used as a counter electrode. All electrolytic solutions were purged with N_2 for 15 min to remove any dissolved oxygen and a nitrogen stream was maintained during the experiment. All experiments were performed at room temperature.

2.1.1. Glycerol electrooxidation

The GEOR in alkaline solution was carried out using Hg/HgO (Koslow Scientific Company) reference electrode. The electrolyte solutions were prepared from KOH (EMD, ACS grade), Glycerol (Sigma-Aldrich≥99%), and ultrapure de-ionized water (Milli-Q® Millipore, 18.2 MΩ cm at 293 K). Cyclic voltammetry (CV) and chronoamperommetry (CA) measurements were carried out before and after the electrochemical treatment in 1 M KOH and in 1 M KOH + 0.1 M glycerol. The scan rate was 50 mVs^{-1}.