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Electrochemical activity of Nickel Raney nanoparticles with applications in fuel cells

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The electrochemical properties for Ni Raney alloy were investigated related as potential applications in the fuel cells for low operating temperature conditions. The study compares two types of Ni-Raney where nickel powder as raw materials is in micron size, respective synthesized in microwave reactor. Nano-sized Ni Raney showed an increased catalytic activity when its grain size is below 150 nm. Cyclic voltammetry evaluated the electrochemical activity of the of both Ni-Raney structures showing an oxidation potential decreased from 703 mV to 203 mV.

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1. Introduction

The fuel cell performance is strongly dependent on the electroatalyst activity related to a couple fuel-oxidant. Its electrocatalytic activity is mainly dependent on composition, structure, and nanoscale geometry. These characteristics rise to high density of active sites [1]. There is a large variety of electrocatalysts used in fuel cells, each of them being appropriate with the specific working condition and the couple fuel-oxidant. In this respect Nickel-Raney large used in chemical industry was less exploited in fuel cells. Ni- Raney catalysts were first introduced in 1924 and since then they have attracted much attention for hydrogenation of organic compounds due to their inexpensive high-surface area substrates and high catalytic activity. Ni-Raney by its geometry and porous structure play a double role: as electrode and as electrocartalyst being suitable for anode in fuel cells (Proton Exchange Membrane Fuel Cell - PEMFC, Alkaline Fuel cell - AFC etc). Ni- Raney catalyst is usually obtained from binary Ni-Al alloy or Ni-Zn alloy with 40 to 60wt% nickel, in which the Al or Zn are removed with NaOH or KOH by alkaline dissolution, leaving behind a high surface area known as nickel ‘‘skeleton’’ or nickel “sponge” [2,3]. This type of alloy is often prepared by pyro-metallurgical methods at high reaction temperatures. It presents several nickel–aluminium phases (Al_3Ni, Al_3Ni_2, AlNi and Al-Al_3Ni eutectic) [4] or nickel-zinc, phases which are changing with the chemical composition and the preparation method of the alloy [2]. The chemical reaction is schematically written as [5]:

$$2(\text{Al-NI})_{(s)} + 2OH^- + 6H_2O \rightarrow 2Ni + 2Al(OH)_{4\text{-}(aq)} + 3H_{2(g)}$$

The new approach in the preparation of Raney nickel catalysts is referred to the influence of the morphological nature of the metal on the Ni-Raney final proprieties. One of the candidate methods for controlling the proprieties of metal powder is the wet chemical reduction method. Therefore, due to the good solubility of nickel salt in water and low reaction, the morphology of nickel powder such as the shape, the size, and the size distribution of particles, can be easily controlled by reaction parameters, solvent composition, a nucleation agent, a reduction agent, and a surfactant, etc. In this way the preparation of fine nickel powder can be realized using microwave hydrothermal method from the aqueous solution of nickel salt [6].

The aim of this contribution is to analyze the electrochemical behavior for two type of Ni-Raney based on micron-sized and nano-sized nickel obtained by microwave synthesis.

2. Experimental

2.1 Materials

Micron-sized Nickel powder: grain size <0.15 microns, 99.999%, supplied by Ventron

Aluminium powder, 1-5 microns, 99.99% trace metal basis supplied by Pometon S.A

Nickel (II) Chloride, $NiCl_2 \times 6H_2O$, 98%, analytical grade

Other materials: Polyvinylpirrolidone (PVP) (Merck), Ethanol ACS 96% (Ridel-de-Haen), NaOH (Lachema), N_2H_4 (Fluka). All reagents were used as received.

2.2 Preparation of nanosized Ni

Nickel chloride hexahydrate was submerged in alcohol water solvent (60 ml distilled water and 40 ml ethanol). In the starting solution were added 0.4 g PVP as surfactant. After stirring for 15 min, NaOH 6M was used in order to control the pH solution to be 12.0. Finally the solution was reduced with 8.01g $N_2H_4{\cdot}H_2O$ by continuously stirring and heated in reflux at 80 ^{0}C for 7 min in a microwave reactor. The precipitate was recovered by vacuum filtration, and washed in distilled water until the pH 7. The washed precipitate was dried at 80 ^{0}C for 24 h.

2.3 Preparation of Ni-Raney

Skeletal Raney-type catalysts were prepared from Ni-Al alloys with Ni obtained from two different sources (micron-sized Ni and nano-sized Ni resulted by microwave synthesis). The nominal active metal mass contents in the alloys are 50 wt% nickel and 50% aluminum. The two metals were mechanical homogenized and shaped in disc form by molding at 5 tf/cm^2.

The Ni-Al discs were thermal treated at 750 ^{o}C for 5 h (the temperature rised with a rate of 2.2 ^{o}C/min for 3h, kept at 400 ^{0}C for 30 min, and for another hour the temperature rised to 750 ^{0}C h) in argon atmosphere. After the pyro-metallurgical step, the Al–Ni disc was activated by leaching out the aluminum with NaOH 1M at room temperature for 3h. The catalysts were subsequently washed several times with distilled water and dried at 70 ^{0}C for 1 h. Two set of samples were prepared: standard Ni-Raney using micron-sized Ni and nano-sized Ni, respectively.

2.4 Characterization methods

Optical microscopy: metallographic microscope, Biostar Model, Digital Camera Canon, Magnification 1000 x.

Electronic microscopy: Scanning electron microscope TESCAN, resolution 1 nm

Cyclic voltammetry: For measuring the electrochemical activity, a 3 electrode cell was used (potentiostat VoltaLab PGZ 301, Radiometer) at room temperature: Pt-auxiliary electrode, Standard Calomel Electrode (SCE) XR110 as reference electrode and the sample (Ni- Raney) as working electrode. Measurements were performed at a scanning rate of 100 mV/s, in the range [-0.6; 1] V for the standard Ni- Raney disc and [-0.1;1]V for the nano-sized Ni- Raney disc using a 0.5M H_2SO_4 solution as electrolyte.

3. Results and discussion

Microscopy and composition. The morphology of the Ni nanoparticle micron-sized shape are usually spheroidals. In opposite Ni nanoparticles obtained in microwave develop on their surface small and randomized crystallographic planes (Fig. 1).

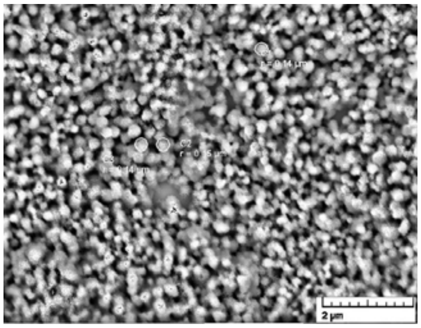

Fig. 1. SEM micrograph for Ni synthesized in microwave reactor. Topography reveals nanoparticles with average dimension of 130-140 nm where (111) and (100) crystallographic surfaces are equal distributed on the nanoparticle surfaces.

Optical microscopy reveals a typical morphology of the Skeletal Ni Raney catalyst. It should be noticed that the amount of Aluminium is higher in the nano-sized Ni Raney disc, and the residual alumina left after leaching will act as a structural promoter, stabilizing the catalyst, as reported elsewhere [7,8]. The residual quantity of Al in the two Raney Ni discs depends on the Ni and Al particle dimension and the morphological properties of the metals. The two discs present small amounts of intermetallic phases, revealing comparatively discontinuous change of composition in product layer: Ni_2Al_3 and $NiAl_3$ [7]. Because $NiAl_3$ is known to be much more reactive toward alkali than Ni_2Al_3, the discs are presenting a higher quantity of Ni_2Al_3 than $NiAl_3$. In Fig. 2 are shown optical microscopy for standard Ni-Raney and that with Ni synthesized in microwaves. Fig. 2a reveals a large and heterogeneous distribution of the metallic phases Ni_xAl_x specific for given pyro-metallurgical conditions. The grain size is not homogeneous. In opposite, when Ni is synthesized with microwaves the alloys developed in the Ni-Raney disc are more homogeneous, with a uniform porosity (Fig. 2b).

Cyclic Voltammetry. Ni-Raney standard (Fig. 3a) shows a weak oxidation (E_a=703 mV, j=7.035 mA/cm^2) and reduction potential (Er=106 mV, j=-4.56 mA/cm^2) at a scanning rate of 100 mV/s, in the range of -0.6 to 1V.

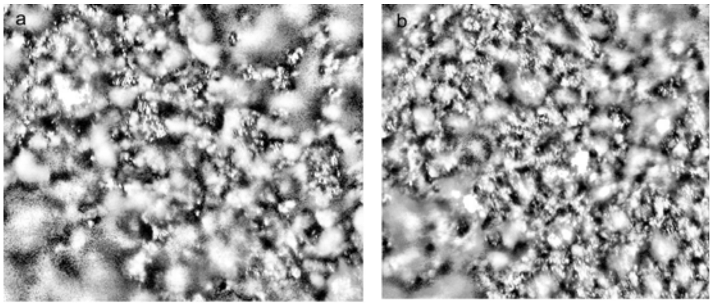

Fig. 2. Optical microscopy (40x), (a) Standard Ni Raney disc; (b) Nanosized Ni Raney disc.

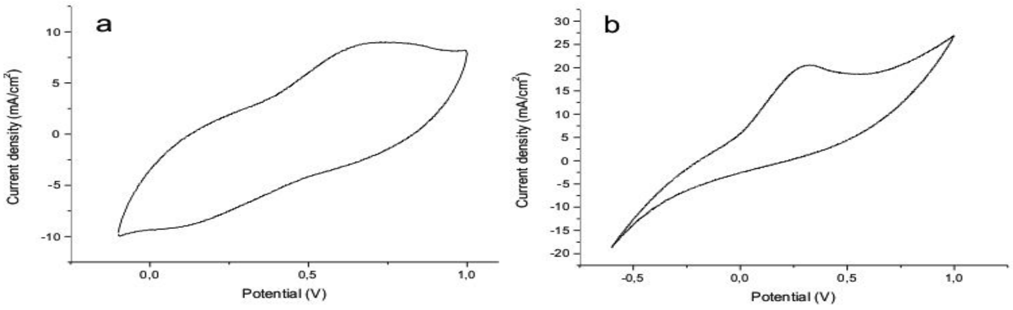

Fig. 3. CV response vs SCE, for Ni Raney coated in 0.5 M H_2SO_4. (a) conventional Raney Ni response; (b) nanosized Raney Ni response at the scan rate of 100 mV/s.

The total specific charge transfer (Q_T) for the Conventional Ni Raney sample was calculated as follow:

$$Q_T = \frac{1}{\nu}\int_{E_i}^{E_f} \left(I_a - I_c\right)\, dE = 7.54 mC / cm^2$$

where υ is the sweep rate of 100 mV/s, I_a and I_c are the current density for anodic (oxidation) and cathodic (reduction) peak and E is the potential.

The nanosized Raney Ni catalyst shows only an oxidation peak on the anodic component (Ea = 278 mV, j=11.61 mA/cm^2) (Fig. 3a) at a scanning rate of 100 mV/s, in the [-0.1;1]. In the absence of electrolysis the oxidation peak vanished and the probe has a week electrochemical response, without oxidation or reduction. The nano-sized Ni Raney has a total specific charge transfer value of Q_T=42.48 mC/cm^2.

The double layer capacity of the conventional Ni Raney is 80.10 mC/cm^2. This value is smaller than the double layer capacity of the nano-sized Ni Raney, 101.52 mC/cm^2. This fact leads to the conclusion that the nanosized Raney Ni is a good catalyst, and can be succefully used as anod in hydrogen fuel cells.

4. Conclusions

Nano-sized Ni Raney catalyst shows a promising way to be used as catalyst at lower temperatures compatible with the working conditions for PEMFC. In addition the microwaves synthesis has proved to be a suitable method to design nanosized powder with appropriate morphology and high surface activity for electrocatalyst. In this respect nano-sized nickel obtained by this method can be used for designing different types of Ni Raney alloys with specific catalytic activity.

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