

FeNi cathalyst for polymer electrolyte fuel cells

S. STAMATIN*, A ANDRONIE, C. CRISTESCU, S. M. IORDACHE, A. CUCU,
C. LUCULESCU^a, C. CEAUS, I. STAMATIN

University of Bucharest, 3 Nano-SAE Research Centre, Bucharest, Romania,

^aNational Institute for Laser, Plasma and Radiation Physics, Magurele, Romania

Polymer electrolyte fuel cell (PEMFC) with FeNi cathode electrocatalyst is studied as an alternative to commonly used platinum and/or its alloys. A simple geometry with Pt particles deposited on carbon paper by ink spraying and thermal evaporated FeNi alloy on carbon paper are pressed on fluorosulfonated membrane in a membrane electrode assembly and tested in PEMFC hydrogen-air. Open circuit potential function of hydrogen-air pressure measured at 60°C- set point and 90% relative humidity reached 510 mV for 200KPa hydrogen and air pressure.

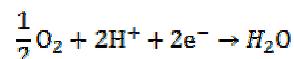
(Received April 7, 2010; accepted April 26, 2010)

Keywords: Fuel cells, Iron-nickel catalyst, Polymer, Electrolyte

1. Introduction

The conversion of chemical energy in useful work and heat from a couple fuel-oxidant has been a big challenge for centuries. Representative in field is fuel cell, an electrochemical device that converts chemical energy of supplied fuel and oxidant directly into electrical energy and, as products, water and heat. A subclass is Proton Exchange Membrane Fuel Cell (PEMFC). The heart of PEMFC is the membrane electrode assembly (MEA) made of proton conducting polymer coated on both sides with electrocatalyst for the fuel oxidation to anode respectively for the oxidant reduction to cathode [1]. Pt is the most commonly used catalyst for PEM fuel cell. Nevertheless there are some important drawbacks: CO poisoning at very low concentration (ppm), costly and limited resources. Hydrogen containing CO generates a serious problem as CO is irreversibly absorbed on active site at Pt surface blocking hydrogen absorption and lowering the reactivity of the remaining available sites by dipole interaction and electron capture [2]. Early reports on the use of Pt alloys for a CO tolerance increasing, include Pt-Ni, Pt-Co, Pt-Cr, Pt-Mn and Pt-Fe [3]. A composition of 75(Pt):25(M) (M stands for non-noble metal) was found to be optimal [4]. Johnson Matthey found out that a 50:50 Pt-M ratio improve the activity if they were heat treated at different temperatures [5]. It was found that an improvement of 20-40 mV could be obtained if Pt-Ti, Pt-Mn and Pt-Fe are used as electrocatalysts in PEMFC.

Ni, Fe and their alloys respectively, compounds are also well known catalysts. The most important opportunity for fuel cells applications is electrocatalyst for oxidant reaction reduction (ORR) to the cathode layer (CCL) where protons out of membranes with electrons coming from external electrical circuit meet oxygen with output water and heat by the following chemical reaction:



To evaluate performances as electrocatalyst for FeNi (60/40) alloy in PEMFC, a series of measurements were performed on a specialized testing bank with facility to rise voltage in open circuit and polarization curve for different set points.

2. Experimental

2.1 FeNi Catalyst deposition

FeNi alloy (60/40) was deposited by thermal evaporation on 30x30 mm teflonated carbon paper (PTF-50, carbon paper made of carbon fibers purchased from Ballard). Thermal evaporation was performed with VUP 5-M vacuum universal deposition equipment in N₂ atmosphere at 6×10^{-5} and Ta pan. A total amount of 0.3 mg FeNi was deposited on carbon paper surface target within 40min at a temperature of 1500-1550 °C, close to the melting point (~1450°C). The low evaporation rate leads to a well-developed microstructure with composition close to the initial one.

2.2 MEA assembling and fuel cell operation

The perfluorosulfonated polymer membrane - Fumapem 1050 (source Fuma-Tech, GmbH) was treated and conditioned to acidic form [6]. Anode electrode was prepared by usual ink spraying technique of Pt on carbon paper [7]. The amount of Pt deposited on carbon paper was 0.5mg on a 30x30 mm area. Anode- Pt and cathode- FeNi carbon papers coated with electrocatalysts were hot pressed on the membrane at 130°C at 20KPa to obtain MEA. Finally, MEA was assembled between two graphite plates with channels for fuel/ oxidant feeding and heating

system. Each site is connected to a saturator for membrane humidification, which reaches a maximum proton conductivity of 100mS/cm at 90% RH and 60°C operating temperature.

2.3 Characterisation techniques

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

Electronic microscopy: Scanning electron microscope FEI Inspect S Model with EDAX module SiLi detector EDAX Inc.

Cyclic voltammetry: For measuring the electrochemical activity, a 3 electrode cell was used, potentiostat VoltaLab PGZ 301: Pt XM140 as auxiliary electrode, Ag/AgCl XR310 as reference electrode and the sample (NiFe) as working electrode. Measurements were performed at different scanning rates: 100 mV/s, 50 mV/s,

25 mV/s, 10 mV/s, respectively 5 mV/s, in the range [-0.1; 0.9] V at room temperature using a 0.5M H₂SO₄ solution as electrolyte purged with nitrogen.

Fuel cell testing system: model BT-512 (Bekktech LLC, USA) multifunctional system with saturator, hot plates made of graphite with inner channels for gas access, electronic load box, fueling circuits for hydrogen and oxygen/air in the range 1-5 bar [8].

3. Results and discussion

Microscopy and composition. Optical microscopy reveals a typical morphology of the FeNi thermal evaporated on carbon paper. Small particles are deposited on the microfibrillar structure of the carbon paper. At the interception of two fibers, particles grow by merging each other developing a thin film that covers the free space between fibers (Fig. 1).

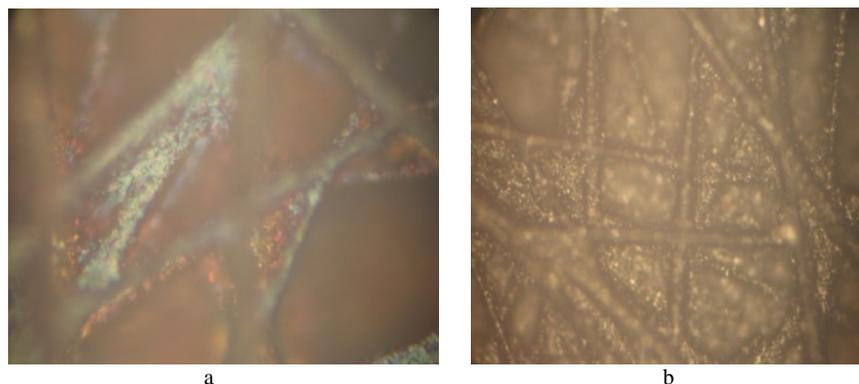


Fig. 1. Optical microscopy (40x), FeNi films (a) grow on fibers and interfibers at their interception (b).

A detailed morphology at down scale investigated by SEM a cobweb of films interfibrillar developed (Fig. 2a). When the interfibrillar distance is under a critical limit then the film surface has different curvature due to surface

tension (figure 2b). A more detailed analysis a 5 and 1-micron scale (figure 2 c, d) show a wormlike assembling of FeNi grains in microfibrile shapes with very small intergrain voids.

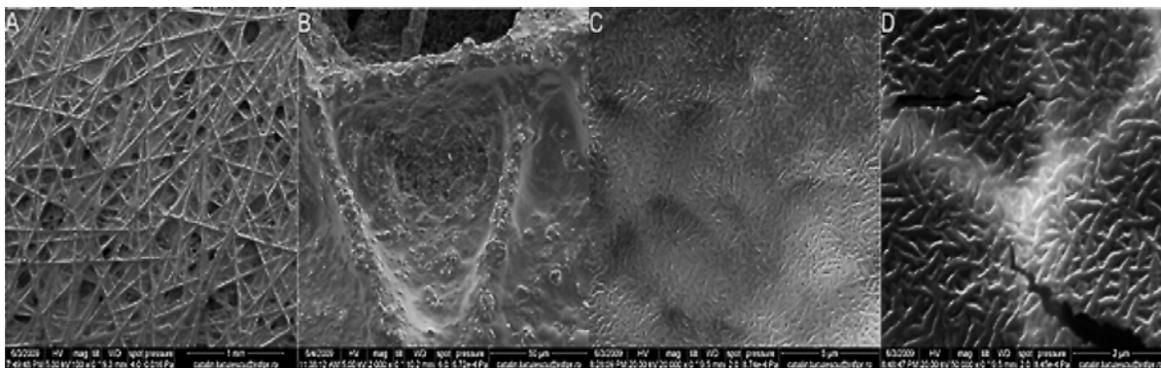


Fig. 2. a) Cobweb of FeNi films interfibrillar grown. b) Films grown in small inter-fibrillar space with different curvature due to surface tension c), d) wormlike and microfibrillar morphology of the FeNi deposited by thermal evaporation.

Compositional analysis performed by EDAX led to Fe/Ni ratio in average 60/40 (+/- 5%) which means the evaporation of the iron-nickel alloy is much more complex than a simple atomic evaporation. It can be concluded that Fe-Ni alloy clusters are evaporated and subsequently deposited on carbon paper. Moreover, substrate temperature can have a large influence on grain size shape and homogeneity of the deposited films.

Cyclic Voltammetry. The FeNi catalyst has a reduction activity around 300-350 mV/s vs Ag/AgCl reference electrode (figure 3). This fact leads to the conclusion that it can be used as a catalyst for the reduction reaction at cathod in presence of oxygen.

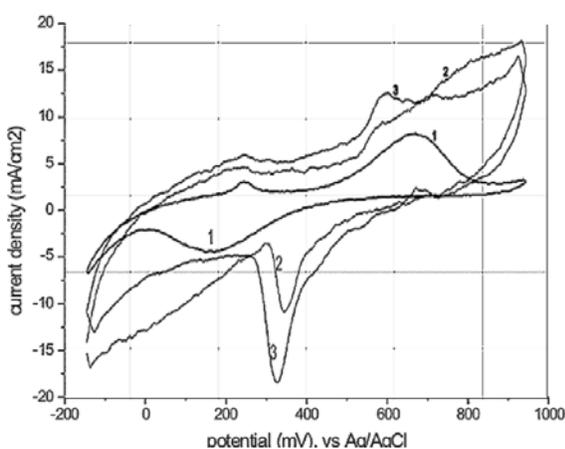


Fig. 3. CV response vs Ag/AgCl reference electrode, for carbon paper with FeNi coated in 0.2 M H_2SO_4 . (1) Carbon paper response, (2) Carbon paper coated with FeNi at scan rate 50mV/s and 100mV/s (3)

Carbon paper, curve (1) on Fig. 3, has a symmetric oxidation and reduction peaks centered on 700mV and 190mV with large irreversibility. When FeNi is deposited on carbon paper, all CVs show a high and tight reduction peak, 320mV, which increases with the scan rate. In addition, the CV has large area that is assigned to a high charged double layer. The oxidation peak from carbon paper moves to lower potential and decreases in value with the scan rate. Plotting for oxidation and reduction current vs. square root of the scan rate (Fig. 4) led to an effective characterization of the electrocatalyst reactivity and the irreversibility of electrode reactions. At low scan rate, processes are in equilibrium up to 25m/s and diffusion processes control kinetics. At higher scan rate, the reduction current increases once with the transport of charges to electrode.

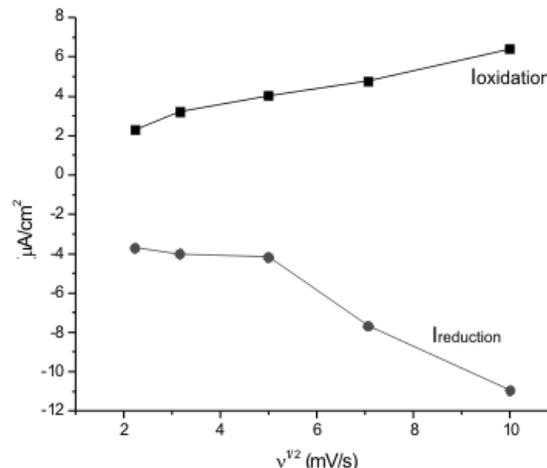


Fig. 4. Current density vs. square root of scan rate. The oxidation is contribution from carbon paper and reduction from carbon paper coated with FeNi.

The FeNi catalyst tested in MEA on the testing bank shows a very interesting behavior taking in account that the amount of catalyst ratio Pt/ NiFe= 1.66 (Fig. 5). At set point 60°C and 90%RH when the air pressure is 30kPa (partial pressure for oxygen, ~8.7kPa), the potential increases constant with hydrogen pressure on the anode up to 390 mV corresponding to 200kPa. Keeping the hydrogen pressure at 200kPa and increasing the air pressure up to 200kPa (partial pressure for oxygen, ~58 kPa) the potential rise to 510mV. These results are in good agreement with that reported when Pt catalyst is used with OCP =600-1000mV function of Pt loading on the carbon paper for both electrodes [9].

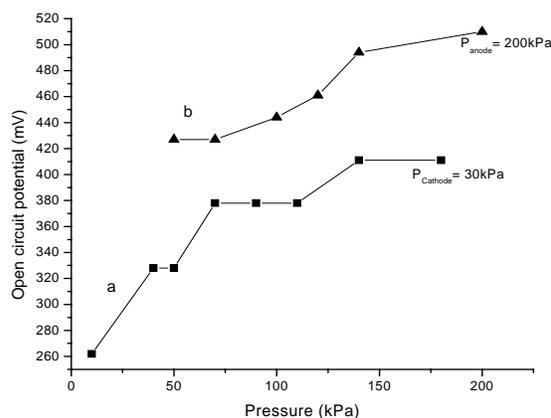


Fig. 5. OCP value for MEA with Pt and FeNi electrocatalysts coated carbon paper. OCP increases with hydrogen and air pressure for a set point of 60 °C and 90%RH.

4. Conclusions

FeNi alloys are promising electrocatalysts for reduction reaction at cathode site in polymer electrolyte fuel cell applications. The OCP reaches 500mV when the pressure of hydrogen and air reach value of 200kPa for a set point of 60 °C and 90% relative humidity on membrane.

References

- [1] JiuJun Zhang, Ed, PEM Fuel Cell, Electrocatalysts and Catalyst Layers, Springer, 2008
- [2] A. F. Inocente, A.C.D Angelo, J Power Sources; **162**, 151 (2006).
- [3] S. Mukerjee, S. Srinivasan, M. P Soriaga, J. Electrochemical Soc. **142**, 1409 (1995)
- [4] U. A. Paulus, A. Wolkaun, G. G. Scherer, T. J. Schmidt, V. Stamenkovic, N. M. Markovic, Electrochim. Acta **47**, 3787 (2002).
- [5] T. R Ralph, M. P. Hogarth, Platinum Metals Rev **46**, 3 (2002)
- [6] Er-Dong Wang, Peng-Fei Shi, Chun-Yu Du, J Power Sources **175**, 183–188 (2008)
- [7] W. Z. Li, C. H. Liang, J. S Qiu, W. J. Zhou, H. M. Han, Z. B. Wei, G.Q. Sun, Q. Xin, Carbon **40**, 787 (2002).
- [8] www.bekktech.com
- [9] Silas Towne, Vish Viswanathan, James Holbery, Peter Rieke, J Power Sources **171**, 575 (2007)

*Corresponding author: office@3nanosae.org