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Review

Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions – A Review

Fariba Safizadeh ^{a,*}, Edward Ghali ^a, Georges Houlachi ^b^a Department of Mining, Metallurgy and Material Engineering, Laval University, Québec, G1V 0A6, Canada^b LTE, Hydro-Quebec, 600 Avenue de la Mortagne, C.P. 900, Shawinigan, QC, G9N 7N5, Canada

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ABSTRACT

This review provides an overview of some important investigations performed on the development of efficient electrocatalysts in the presence of alkaline solutions. The efficient electrocatalysts must encounter different characteristics such as low overpotential for hydrogen evolution reaction (HER), good catalytic activity, high stability and low cost. This review provides basic information, particularly about the development and properties of some of the most investigated electrocatalysts, namely from the iron group elements (iron, nickel or cobalt). A great interest to investigate amorphous alloys can be found in literature because of their superior properties towards HER. Amorphous alloys show many interesting properties such as electrochemical and good mechanical properties along with high corrosion resistance. Molybdenum and phosphorous, as most promising elements offering great amorphization capability, were widely investigated in the literature. The induced co-deposition of molybdenum and phosphorous was particularly considered in this review. Other metal groups such as pure metals, some rare-earth elements etc. were also discussed as alloyed composites. A focus was made on electrodeposition method used for the alloys preparation, especially for chlor-alkali industry applications.

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Introduction

The hydrogen evolution reaction (HER) on different metals in acidic or alkaline media is one of the most investigated reactions in the field of electrochemistry. The HER received considerable attention because; (a) hydrogen is an interesting candidate as an energy carrier for future fuel cells applications, (b) it is one of the main reaction products during chlorine production and, (c) the HER supplies the highly pure hydrogen. The HER is the main reaction developed in alkaline

water electrolysis, hydrogen-based fuel cells, and during some industrial productions such as chlor-alkali and chlorate cells. However, these electrochemical processes consume large amounts of electrical energy because of the hydrogen overvoltage. Hence, the reduction of cathodic overvoltage is of great interest in attempts to minimize energy consumption. A few review papers about HER studies in alkaline solutions were published by Tilak et al. [1], Appleby et al. [2] and Lasia [3]. Various materials were studied to develop the efficient and durable cathodic electrocatalysts to reduce the over-potential of the HER. Application of metals and alloys as higher

* Corresponding author.

E-mail address: Fariba.safizadeh.1@ulaval.ca (F. Safizadeh).
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Nomenclature

HER	hydrogen evolution reaction
η	overpotential
i	current density
A	surface area
b	Tafel slope
i_0	exchange current density
q_1	necessary charge for deposition of a monolayer
θ	fractional coverage
C_ϕ	dependence of the fractional surface coverage and of the electrodeposited species
P	energy consumption
ε	current efficiency, %
CD	current density
E	cell voltage
K_H	Herovskiy rate constant
R_f	surface roughness
Mm	mishmetal
EIS	electrochemical impedance spectroscopy
ANOVA	analysis of variance
R_p	Polarization resistance
CCE	cathodic current efficiency
DSC	differential scanning calorimetry
XRD	X-ray diffraction
RE	rare earth

performance materials for HER received more scientific and industrial attention in the past and still does. Such high-performance electrode materials should satisfy multiple criteria like good catalytic activity, chemical and mechanical stability and low cost [4]. Jaccoud et al. [5] resumed the properties of an ideal electrocatalytic cathode as per the followings: a) low hydrogen overvoltage at industrial current density, b) no potential drift with time, c) good chemical and electrochemical stability: long lifetime and no release of process-deleterious products, d) high adhesion to the support, e) low sensitivity to poisoning by impurities, f) low sensitivity to current shut down (short-circuit) or modulation, g) no safety or environmental problems in the manufacture process, h) easy to prepare at a low cost/life time ratio. Therefore, considering the strict criteria to be satisfied, choosing the most appropriate electrode material is not an easy task.

A good improvement in materials performance used as HER electrodes could be achieved by optimizing geometric factors, i.e., increasing the real surface area and electronic factors, i.e., the change of the Tafel slope. This is a clear indication for the true catalytic effect. Hence, the strategies of choosing high-performance materials in the presence of high alkaline solutions have mainly focused on two aspects: (i) selection of a material exhibiting high i_0 (exchange current density) and (ii) increase of the specific surface area [6].

The energy consumption reduction depends on two important parameters; overpotential (η) and current density (i), that can be shown by the following equation [6]:

$$I/A = i = i_0 \exp(\eta/b) \quad (1)$$

or

$$\eta = b \ln(I/i_0A) \quad (2)$$

where A refers to the surface area, b to the Tafel slope ($d\eta/d\ln i$), and i_0 to the exchange current density. The value of Tafel slope (b) is almost equal to 120 mV on smooth surfaces of metals at 25 °C in alkaline solutions [7]. The materials containing high i_0 and low b are more favorable since they can operate under high current density without a significant increase in the over-potential (Fig. 1).

In this context, noble metals such as platinum and ruthenium are the most active and stable materials, but their extremely high cost and limited abundance are the major obstacles for their industrial applications [8]. Thus, one of the most important goals in modern electrocatalysis is to completely replace Pt by low cost and active catalytic materials. Although non-platinum active metals such as Fe, Ni or Co are considerably cheaper, they suffer from corrosion and passivation under reaction conditions [4]. As such, great efforts are being made in order to improve corrosion resistance and activity of these metals, usually performed by alloying them and modifying their synthesis routes. Alloying different metals can lead to increase the intrinsic electrocatalytic activity, to change of morphology (intrinsic specific surface area) and high corrosion stability. However, the enhancement of electrocatalytic activity for HER can be also influenced by the type of alloying or the method of cathode preparation.

Kinetic studies

In order to better understand the kinetics of cathodic HER, it is necessary to determine the mechanism of the reaction. This is usually done by characterizing the adsorption behavior and surface coverage of kinetically adsorbed intermediates such as hydrogen during hydrogen evolution [9,10]. Many researchers investigated the kinetics of the hydrogen evolution reaction on different materials [10–16].

Some of the techniques, most frequently applied for the kinetic studies are as per the followings:

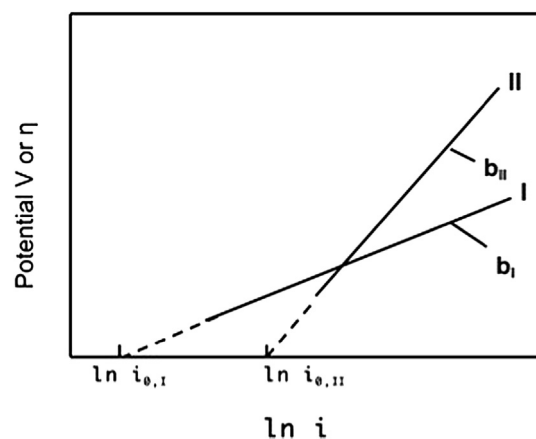


Fig. 1 – Relative polarization behavior of two processes at an electrode having two i_0 and b values. Process I offers better performance at high current density even though the i_0 is low [6].

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