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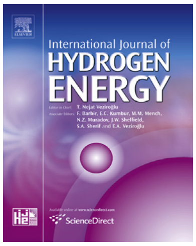

Stable and inexpensive electrodes for the hydrogen evolution reaction

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ABSTRACT

The HER activities of Raney–Ni electrodes obtained by partial leaching of Al in a Ni–Al–Fe alloy doped with Mo, Cr or Pd were studied in 28% KOH. PTFE bonded Gas Diffusion Electrodes (GDEs) were prepared by the rolling method before sintering at 300 °C under N_2. Ni in alkaline electrolyte has a lower intrinsic HER activity than Pt in acid. However, the spongy and highly porous character of Raney–Ni greatly enhances HER resulting in a cheap material with outstanding catalytic performance. The polarization behavior of GDEs consisting mainly of Raney–Ni catalysts with optional addition of co-catalyst or conductivity enhancing powders, such as carbonyl iron, carbonyl nickel, copper and molybdenum oxide are studied as a function of temperature and time in order to determine activities, behavior in the high current density regime, and long term stability in view of potential exploitation in industrial electrolysis. Cr and Pd-doped Raney–Ni initially achieve outstanding performances with unusually low "Tafel slopes". After weeks long cathodic treatments, these GDEs eventually attain inferior but stable activities due to an apparently irreversible aging of Raney–Ni. The aging of Mo-doped Raney–Ni is less conspicuous, and relevant performances are sometimes improved by additives. A clear picture is emerging of the mechanisms controlling polarization and aging behavior of Raney–Ni GDEs. From this picture, suggestions are put forward on how to improve stability and performances of full electrode assemblies and make them suitable for use in advanced alkaline electrolyzers.

1. Introduction

Anthropogenic fossil fuel emissions are the main responsible for the increase of atmospheric CO_2 and associated climatic and environmental changes [1]. Environmentally benign fuels, which can easily substitute fossil fuels in the current energy supply chains are sought. One of these fuels is hydrogen, which many believe to be the energy carrier of the future, and a major option to mitigate greenhouse gases and other environmental problems [2,3]. Hydrogen is today a main substituent and reactant in many important chemical processes as well as in internal combustion engines and in heat

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production. Hydrogen is a very versatile fuel: it may be used as an additive to conventional fuels which improves the performances of the heat engines or as the main fuel for transportation, or directly in fuel cells for efficient power generation. However, introduction of hydrogen would lead to a substantial change in the coupling between energy production and global environment only if H_2 is produced from renewable energy sources [3] leading to emission of only contrails and vapors with no CO, CO_2, hydrocarbons and reduced NO_x. Among the technologies of renewable H_2 production, conventional electrolysis with a renewable power source is technologically more mature than photoelectrochemical water splitting or bio-hydrogen production [4]. Even so, a lot of work is needed to make this technology competitive by optimizing the individual conversion steps which lead from solar energy to, say, a fuel cell driven car [5–7].

Electrochemical water splitting is an old, flexible and apparently mature technology for hydrogen production. The cathodic and anodic reactions of hydrogen evolution (HER) and oxygen evolution (OER) are the most studied in electrochemistry but fundamental investigations of new HER/OER catalysts are being pursued today with renewed intensity both experimentally [8–13] and theoretically [14]. Also the technological developments are actively pursued, with many suggestions being presented regarding recipes to produce practical electrodes with high specific activity and high surface area, which are durable and able to sustain elevated current densities.

The main problems encountered by large scale electrochemical hydrogen production are the system costs, which are prohibitive when one employs platinum-group metal (PGM) catalysts as in proton exchange membrane (PEM) electrolyzers [15], and the relatively inefficient use of electrical energy, which becomes a major drawback when inferior but abundant non-PGM catalysts are used [16–18]. Today, industrial scale production of electrolytic hydrogen is mostly based on alkaline type electrolyzers employing massive mild steel or nickel electrodes with system efficiencies as low as 60% and with investment/maintenance costs which are typically several times the overall energy cost despite the long operational life (~20 years) [19]. An attractive feature of alkaline electrolyzers is that they can be made with inexpensive materials and allow, in principle, optimal combinations of cheap and durable electrocatalysts, compared to PEM electrolyzers which depend highly on PGM catalysts. For this reason, much of the current HER/OER research deals with non–PGM catalysts.

The performance of a practical electrode depends upon its morphology as well as upon the catalysts employed. Imparting the desired nanostructure to the catalysts, sometimes using organic templates, is a means to increase the roughness of an electrode, i.e. the ratio between its electrochemically active area and nominal area [20–22]. Composite electrodes combine materials with complementary properties in order to improve electrocatalysis, conductivity, mechanical and chemical stability, limiting currents.

Among candidate materials for alkaline electrolysis, Raney–Ni obtained from Ni–Al alloys with small concentrations of other transition metals has been used for both OER and HER as well as hydrogen oxidation reaction (HOR) for alkaline fuel cells [23,24]. The HER with composite Raney–Ni electrodes containing combinations of elements (Fe, Cr, Mo, Sn, Co, V, Cu) and compounds (rare earths, nitrides, sulfides) [24–34] have shown increased performances, with substantial suppression of the overpotentials at a given current density, or with larger currents and power densities at a given potential. Various hypotheses such as electronic configuration of Ni alloys, surface properties, phase and/or morphological changes, hydrogen absorption and desorption capacities (weak and strong bonds), mass transport properties and kinetic behavior were thought as the main causes of the improved catalytic activity in the references mentioned above. Moreover, the distinct exchange current densities vs. the various M–H bond strengths (M = metal) in the volcano curve [35] may also be affected by the recombination, alloying and inter-diffusion of the elements in the crevices and cavities of the highly porous structure of Raney–Ni through stabilization and enhancement of the overall catalytic activities.

This study characterizes a range of commercial Raney–Ni catalysts (originally containing Al, Fe with Cr, or Mo, or Pd) in their admixtures with a binder (PTFE) and (optionally) coarse grained additives to control/modify catalytic activity, chemical and mechanical stability, pore size distribution, gas transport, wettability, electric conductivity. Emphasis will be placed upon the long term behavior (aging) of the electrodes and the phenomena of activation/deactivation occurring in continuously and intermittently operated electrochemical cells, i.e. in conditions approaching a real life usage. Indeed, this information is seldom given in the open literature, but it is of paramount importance in view of the technological exploitation of the electrodes. For the same reason, the electrodes have been extensively tested at relatively high currents ($500\ mA\ cm^{-2}$) and temperatures (80 °C) where efficiency and power density of the best cells approach those of PEM electrolyzers.

The Raney–Ni powders and the additives (Carbonyl Fe, MoO_3, Cu powder, Carbonyl Ni or Ni–255) were wet-proofed and bonded with PTFE and integrated into the active layer of a gas diffusion electrode (GDE), which led to electrolyzers having the simple system architecture of an alkaline fuel cell [16]. Commercially available Raney–Ni without treatments and with the additives were used for this study. The preparation technique, described below, does not require expensive equipment and allows much flexibility; it has been implemented in a lab but it is easily scalable. Furthermore, it permits to roll and join different functional layers to achieve the compact and sturdy design of cell configuration, which is the strongest point similar to the Membrane Electrode Assemblies (MEA) used in PEM devices.

2. Experimental

Both single and double-layered gas diffusion electrodes (SLGDE or DLGDE) were prepared by applying a mixture of commercial Raney–Ni with Fe, residual Al and trace amounts of Mo or Cr or Pd purchased from Johnson Matthey with admixtures of Carbonyl Ni, Carbonyl Fe, Cu, MoO_3. The binding agent of these powders was a PTFE water dispersion. The

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