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Development of durable and efficient electrodes for large-scale alkaline water electrolysis

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ABSTRACT

A new type of electrodes for alkaline water electrolysis is produced by physical vapour depositing (PVD) of aluminium onto a nickel substrate. The PVD Al/Ni is heat-treated to facilitate alloy formation followed by a selective aluminium alkaline leaching. The obtained porous Ni surface is uniform and characterized by a unique interlayer adhesion, which is critical for industrial application. IR-compensated polarisation curves prepared in a half-cell setup with 1 M KOH electrolyte at room temperature reveals that at least 400 mV less potential is needed to decompose water into hydrogen and oxygen with the developed porous PVD Al/Ni electrodes as compared to solid nickel electrodes. High-resolution scanning electron microscope (HR-SEM) micrographs reveal Ni-electrode surfaces characterized by a large surface area with pores down to a few nanometre sizes. Durability tests were carried out in a commercially produced bipolar electrolyser stack. The developed electrodes showed stable behaviour under intermittent operation for over 9000 h indicating no serious deactivation in the density of active sites.

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1. Introduction

According to the *World of Energy Outlook 2010*, made by the International Energy Agency, renewable energy is the answer for a more secure, reliable and sustainable future. This implies that a higher percentage of the energy will have to come from fluctuating renewable energy sources such as wind, sun and water. Simultaneously, the ever increasing demand and stronger legalisations towards reducing the CO₂ emission worldwide [1] makes it necessary to develop new efficient alternatives for energy conversion, energy storage and load management. Using the excess electrical power from renewable energy sources, e.g. wind, solar and wave technologies, to produce hydrogen via water electrolysis, offers the possibility

of increased production capacity and load management with no greenhouse emissions. The hydrogen can subsequently be stored and used for producing electricity via fuel cells, combustion engines or gas turbines, whenever needed. New ideas for using hydrogen as a raw material for production of synthetic fuels, such as methane by the Sabatier process [2], liquid fuels by the Fischer–Tropsch synthesis [3] or simply pumping the hydrogen gas into the existing natural gas infrastructure, the “power-to-gas” idea will suddenly be a reality when hydrogen becomes available in large quantities [4].

A variety of water electrolysis systems have been proposed and constructed over the years. Alkaline electrolysis is the most mature commercial water electrolysis technology and offers the advantages of simplicity and is the current standard

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for large-scale water electrolysis systems [5] [6]. However, finding low cost electrode materials that are both efficient and durable is one of the remaining challenges for alkaline water electrolysis (AWE) techniques.

Traditionally, the cathode material for AWE systems was made of steel and the anode material from nickel or nickel-coated steel [7]. The pioneer work of Paul Sabatier (1912) and Murray Raney (1925) on hydrogenation catalysts [8] enabled Justi and Winsel to discover the highly porous Raney nickel as an efficient hydrogen electrocatalyst in an alkaline media already in 1961 [9].

Raney nickel catalysts are generally prepared by rapidly cooling a molten solution of nickel and aluminium. The cooling procedure controls which Al–Ni phases are formed in the solid. After solidification, the product is crushed into a fine powder. The catalyst powder is subsequently activated by selectively leaching aluminium from the Al–Ni alloy [10]. Lattice vacancies formed when leaching causes large surface areas and high density of active sites due to a high density of reactive lattice defects [11]. The activated catalyst therefore provides superior performance compared to unactivated non-porous nickel cathodes.

Plasma spraying leachable precursor alloys (Al_3Ni and/or Al_3Ni_2) onto a nickel or steel support is an alternative and common technique applied when producing supported Raney nickel electrocatalysts for alkaline electrolysis [12–19]. Cold rolling and hot dipping of aluminium combined with a thermo-chemical diffusion process have also been proposed [8] [20]. However, the reproducibility and durability of the Raney nickel electrodes are often deficient [7].

When utilizing atmospheric plasma spraying (APS) to form supported Raney nickel electrodes, formation of the electrical resistive and brittle Al_2O_3 phase cannot be avoided. During vacuum plasma spraying (VPS), no oxygen is available to react with the aluminium, and the initial Raney nickel structure appears to be highly active towards the hydrogen evolution reaction (HER) [18]. Producing a VPS Raney nickel structure with interlayer adhesion that can withstand the harsh gas erosion during AWE is however challenging.

In this paper, we report studies on large-scale production of electrodes suitable for commercially available alkaline water electrolysis stacks. The electrodes are produced by plasma vapour deposition (PVD) followed by a thermo-chemical diffusion process and alkaline leaching. Structural characterisation of the electrodes is performed by high-resolution scanning electron microscope (HR-SEM). The electrocatalytic activity of the developed electrodes is studied with steady-state electrochemical measurements and cyclic voltammetry. Durability tests are carried out in an industrial scale-electrolysis stack.

2. Experimental

2.1. Preparation of electrodes

Commercially available nickel plates with a thickness of 0.5 mm were used as an electrode substrate. The purity of the nickel plates were determined by optical emission spectroscopy, detecting 99% Ni, 0.25% Mn, 0.14% Fe and 0.11% Al. Other

residual elements were determined to be below 0.1%. The nickel plates were cut to form circular specimens with a diameter of 3 cm, intended for small-scale electrochemical measurements and scanning electron microscope investigations. 16 nickel plates, designed for a commercial bipolar electrolysis stack, were prepared from the same type of nickel. All nickel specimens to be Al PVD treated were cathodically degreased for 2 min prior to the PVD process. The Al PVD was done in a non-reactive DC-magnetron sputtering mode using a CC800/9 SiO_x coating unit from CemeCon AG. The Ni substrates were heated and etched in situ by Ar sputtering prior to sputter-depositing aluminium to remove nickel oxide (NiO) from the surface. The circular specimens were coated on one side, whereas the specimens for the electrolysis stack were coated on both sides. The thickness of the aluminium coating ranged from 20 to 40 μm . The Al PVD plated specimens were subsequently heat treated in an atmospheric furnace for 24 h at 610 °C followed by a selective aluminium leaching.

Two circular specimen were leached according to the following procedure; 2 h in 1% NaOH at room temperature, 20 h in 10% NaOH at room temperature and 4 h in 30% NaOH at 100 °C, respectively. These specimens will be referred to as PVD Al/Ni 1. Two circular specimens were leached in 30% KOH and 10% $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ at 80 °C with stirring for 24 h. These specimens will be referred to as PVD Al/Ni 2. The aluminium leaching procedure for the 16 large electrodes was identical to the leaching procedure for the PVD Al/Ni 2 specimens.

2.2. Structural characterisation and composition

For cross section characterisation and composition analyses, four PVD Al/Ni specimens, one as plated, one from each leaching method and one unleached, were cut into $1 \times 1.5 \text{ cm}^2$. Each specimen was hot-mounted in CloroFast resin and grinded down to 4000 grit, subsequently polished with 3 μm diamond and 0.04 μm SiO_2 particles. JEOL JSM 5900 scanning electron microscope (SEM) was used for the cross section investigations and an integrated energy-dispersive X-ray spectroscopy from Oxford Instruments was used for elemental analysis. The surface structure and morphology of the PVD Al/Ni 2 electrodes were characterized by means of a FEI Quanta 200 ESEM FEG scanning electron microscope.

2.3. Electrochemical measurements

The catalytic activity of the developed electrodes was evaluated by means of potentiodynamic polarisation curves. The electrocatalytic active surface area of the electrodes was determined by the amount of Ni hydroxide formed during cyclic voltammetry. The measurements were carried out using Gamry Reference 3000 potentiostat/galvanostat and a three-electrode electrochemical cell made of teflon. The reference electrode was a Hg/HgO electrode from Radiometer and the counter electrode was made of pure nickel. The electrolyte contained 1 M KOH and the measurements were operated at 25 °C. All the electrochemical measurements were IR-compensation by means of current interruption technique. All following potentials are specified against the standard hydrogen electrode (SHE) potential.

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