Low-cost AEM water electrolysis with flat stainless steel electrodes

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The work presents a newly developed water electrolyser with AISI 316L stainless steel flat electrodes and anion exchanged membrane (AEM). The electrochemical behavior of AISI 316L is investigated in 25% KOH solution applying the methods of cyclic voltammetry and polarization curves. A single membrane electrode assembly (MEA) is prepared using the stainless steel flat sheets for both the cathode and anode and AB-PBI membrane. The MEA performance is tested by chronoamperometry at constant voltage 2.6 V. Finally, a small electrolyser stack with 4 MEAs is constructed and long-term electrolysis tests are performed. The stack with the AISI 316L electrodes demonstrates stable electrochemical behavior during 600 hours of operation and sustainable performance under a "start–stop" stress test procedure.

Keywords: Water electrolysis, stainless steel, stack measurements, anion exchange membrane

INTRODUCTION

The water electrolysis in cells with anion exchange membrane (AEMEC) is a new alternative for electrochemical production of clean hydrogen. The method offers several advantages in comparison to the classical alkaline water electrolysis such as higher current density, lower ohmic resistance, possibility to operate under high pressure, etc. It has also some benefits compared to the contemporary electrolysis cells with proton exchange membrane electrolyte (PEMEC), among which the most important are the enhanced kinetics of the partial electrode reactions, particularly of the oxygen evolution reaction, and the possibility to operate with non-noble catalysts which makes the technology much more cost efficient [1,2]. The main working unit for both AEM and PEM electrolysis cells is the membrane electrode assembly (MEA), consisting of two electrodes attached to and separated by a polymer electrolyte membrane [3,4]. The design and structure of the electrodes have strong influence on the energy efficiency and service life of the MEA. The electrodes typically have a complicated sandwich configuration with at least two sub-layers: gas diffusion layer (GDL) and catalytic layer (CL) [5]. The nature of the proceeding redox reactions in AEMEC allows the use of a metal mesh as gas diffusion layer. On the top of the GDL, usually highly active catalysts are spread out in the form of thin homogeneous catalytic layer. The catalysts for both partial reactions are mainly non-noble transition metals from the transition series of the periodic table and their alloys. Ni has demonstrated good catalytic properties concerning hydrogen

evolution reaction (HER), while in regard to the oxygen evolution reaction (OER), various Ni-alloys (with Mo, Co, Fe, P, etc.) in different ratios of the components are used [6-8].

Another major problem of AEM water electrolysis is the short life of the electrolyte membrane. The available commercial products are not capable to withstand elevated temperatures [9, 10]. Moreover, they are not stable at the high KOH concentrations required to ensure high ionic conductivity, respectively high energy efficiency of the AEMEC. Recently, the membranes based on poly-benzimidasole (PBI) such as AB-PBI or para-PBI are often used in various fuel cells applications showing good ionic conductivity [11,12]. The complication with this type of membranes is that the pre-conditioning procedure (doping of the polymer skeleton with electrolyte before usage) takes a lot of time and leads to problems with the mechanical preparation of the MEA.

In this work we have investigated stainless steel AISI 316L as potential suitable electrode material for both cathode and anode in AEMEC. This material is broadly used in the hydrogen combustion engines, as well as in the hydrogen-oxygen generators where the produced hydrogen and oxygen (molar ratio 2:1) are not separated. The steel contains about 10 - 14% of Ni and other doping elements and is resistant to corrosion in concentrated alkaline solution. Therefore, it was of interest to investigate its electrochemical activity toward electrolysis of water in AEMEC, as well as its stability at high voltages.

EXPERIMENTAL

The AISI 316L flat electrodes were sized and

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shaped using a laser cutting machine. The geometric area of both cathode and anode was 5 cm². The first series of tests aimed to investigate the AISI 3016L electrochemical behavior in alkaline environment at room temperature. The electrolyte was an aqueous solution of potassium hydroxide (25 wt.% KOH). A three-electrode electrochemical cell with standard hydrogen reference electrode and Pt-wire counter electrode was used. The working area of the test electrode was 1 cm². The experiments were performed applying classical cyclic voltammetry and steady state polarization techniques.

In the second test series, anion exchange membrane was used as electrolyte. The experiments were carried out in a self-designed electrolysis cell, firstly in a single cell mode (fig. 1), and then in a small laboratory stack with 4 single cells (fig. 2).



Figure 1. Picture of a self-designed single AEM electrolysis cell



Figure 2. Picture of a small laboratory AEM electrolyser with 4 single cells

The cell/stack gaskets were made from a 4 mm thick oil-protective rubber. Cyclic voltammetry and quasi-steady-state polarization curves were recorded using Bank Electronics POS₂ potentiostat/galvanostat. Long-term chronoamperometry tests were provided by means of power supply Voltcraft PPS - 1350 connected to photovoltaic panels.

RESULTS AND DISCUSSION



Figure 3. Cyclic voltammogram of AISI 316L stainless steel electrode in 25% KOH; potential range -0.6V - 1.6 V (vs. RHE); scan rate 50 mV.s⁻¹

The cyclic voltammograms of AISI 326L flat electrode recorded in aqueous alkaline solution in the water window potential range are presented in fig. 3. Two well depicted current peaks are seen on the cathodic branch of the voltammogram. The first one which appears at about 1.2 V is related to reduction of oxygen. The second one (at about -0.15 V) is much broader and is due to adsorption of hydrogen on the electrode surface. The hydrogen evolution reaction (HER) starts at -0.47 V and at the applied cathodic potential limit (-0.6 V) the current density reaches 50 mA.cm⁻². The reverse potential scan results in hydrogen desorption peak on the CV at 0.25 V and a broad shoulder in the potential range above 1.25 V, reflecting the formation of adsorbed oxygen-containing species on the electrode surface. The oxygen evolution reaction (OER) starts at 1.45 V, its rate increases rapidly and at the applied anodic potential limit (1.6 V) reaches 60 A.cm⁻². The electrochemical response of the stainless steel electrode does not change during the applied continuous potential cycling. The CVs recorded during the 2nd and 120th cycles are identical, indicating stability of the material under study at the chosen test conditions.

In order to assess more accurately the rate of both partial electrode reactions on the AISI 316L stainless steel electrode, quasi-steady-state polarization curves were recorded (Fig. 4).



Figure 4. Polarization curves of AISI 316L stainless steel in 25% KOH; scan rate 1 mV.s⁻¹

The cathode reaction of hydrogen evolution (in blue) starts at a potential of about -0.4 V and the current density reaches a value of 45 mA.cm⁻² at a potential of -0.6 V. The oxygen evolution reaction (in red) starts at a potential of 1.4 V and the current density reaches a value of about 20-25 mA.cm⁻² at 1.55 V. The further increase of the applied anodic potential leads to transport limitations and the current density reaches limited value.

The results obtained in 25% KON proved the efficiency and stability of AISI 316L as electrode material for electrochemical water splitting. Further, the stainless steel electrodes were integrated in a membrane electrode assembly using anion exchange membrane and tested in a single AEMEC (fig. 1).

Figure 5 presents the MEA performance at conditions of intensive oxygen evolution. A constant cell voltage of 2.6 V was applied for 8 h. Then the voltage was switched off and the cell was left at open circuit potential for another 8 h. The start-stop procedure known also as "stress-test" was repeated continuously in order to assess the longterm performance of the electrolysis cell. The demonstrated results obtained а stable electrochemical behavior for 70 h. When the voltage is switched-on, the current density reaches immediately a value of 0.4 A.cm⁻² and stays constant during the whole test duration. The increase of the start-stop cycles does not lead to changes in the cell performance.

At low voltages the polarization curves of the MEAs differ essentially as those in the middle of the stack show lower current densities. At higher voltages the differences gradually disappear. At stack voltage of 12 V the performance of all 4 MEAs is nearly identical - cell voltage of 3.0 V and current density of about 0.3 A.cm⁻². In order to investigate the stack performance during long term

operation, it was connected to a power supply Voltcraft PPS-1350 at constant stack voltage of 10.2 V.



Figure 5. Long-term stress-test of a single AEMEC

The developed membrane assembly was extended in a small laboratory stack with 4 electrochemical cells connected in series (fig. 2). The performance of this small electrolyser was investigated by quasi-steady-state polarization tests. The recorded polarization curves of each single MEA and that of the whole stack are presented in figure 6.



Figure 6. Polarization curves of a small laboratory AEMEC stack with 4 cells

The obtained results are presented in figure 7. For each single cell in the stack the current density reached value of about 50 mA.cm⁻² and the measured voltage was 2.6 V. The electrolyser demonstrated stable electrochemical behavior for 600 h of operation.



Figure 7. Long-term performance of electrolyser stack with 4 single cells

CONCLUSIONS

The AISI 316L stainless steel demonstrates moderate catalytic activity toward both HER and OER during electrochemical water splitting in electrolysis cell with anion exchange membrane. The material has an excellent stability under dynamic long-term test conditions and sustainable electrochemical behavior both in single AEMEC and when integrated in a stack. Further research on preparation of porous GDE based on AISI 316L stainless steel aimed to increase the active surface and efficiency of AEM electrolysis is in progress.

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