Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effect of Electrochemical Cell Design on the Ionic Conductivity and Oxygen Permeability Determination of Gas Separators

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ARTICLE INFO

Article history: Received 2 December 2013 Received in revised form 3 February 2014 Accepted 4 February 2014 Available online 15 February 2014

Keywords: Gas separator Ionic conductivity Electrochemical impedance spectroscopy Oxygen permeability Mass spectrometry.

ABSTRACT

Electrochemical properties of gas separators, holding a potential for the application in alkaline electrolysis, such as ionic conductivity and impermeability for hydrogen and oxygen gases, are significantly influencing the efficiency of alkaline electrolysis. Both non-zero gap and zero gap atmospheric pressure laboratory scale test set-up, operating at room temperature, were developed in order to undertake a comparative study of their advantages and disadvantages for the lab scale electrochemical characterization of gas separator materials. The zero gap cell was able to provide a more accurate ionic conductivity of the separators via Electrochemical Impedance Spectroscopy (EIS). The non-zero gap cell set-up, coupled with Quadrupole Mass Spectrometer (QMS), enabled the quantitative assessment of the oxygen crossover of different separators. The influence of a long term immersion in 25 wt. % KOH determined using the non-zero gap cell, showed increased conductivity with immersion duration for asbestos, while the highly hydrophobic PPS and PPS with PTFE separators' conductivity was not affected by longer immersion. © 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Today, hydrogen is already used on a large industrial scale and is becoming more competitive as an alternative energy career. Alkaline water electrolysis uses available, low-cost materials and as a process may play an important role for both small and large scale energy consumers, through a distributed energy production, conversion, storage and use system. The accent should be put on the possibility to store the excessive energy from available renewable energy sources in the form of hydrogen by water electrolysis and later on use the stored hydrogen in fuel cells to generate electricity or as a fuel gas. [1,2]

In alkaline water electrolysis [1] (e.g. 25 wt. % KOH), hydrogen (H₂) is produced at the cathode, while oxygen (O₂) is generated at the anode. The overall reaction in alkaline water electrolysis as a sum of the partial reactions can be expressed as follows:

$$H_2 O_{(1)} \to H_{2(g)} + \frac{1}{2} O_{2(g)}$$
 (1)

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http://dx.doi.org/10.1016/j.electacta.2014.02.007 0013-4686/© 2014 Elsevier Ltd. All rights reserved. A separator, which is placed in-between the cathode and anode, limits the crossover of produced hydrogen and oxygen, while still allowing for ions to migrate across reaction sites. Possible candidates for a separator material have to fulfill numerous requirements [3], such as: good gas separation and high ionic conductivity, fast evacuation of the bubbles from the separator's surface, chemical and mechanical stability in 25 wt. % KOH solution at 85 C. Further on, the material should be economically acceptable, environmentally friendly [4], and should provide a long life span.

Optimization of ion conductivity and gas barrier properties, which in fact tend to follow opposite trends, can lead to the improvement of the electrolysis process efficiency [3,5]. Therefore, the aim of this study was to establish the methodology based on electrochemical techniques for determination of these two parameters. The characterization was conducted for asbestos, state of the art separator material in high pressure zero gap alkaline electrolyzers, which use has been banned because of the health related issues [4]. Additionally, polyphenilene sulphide (PPS), used in less stringent electrolysis systems regarding gas purity and PPS with polytetrafluoroethylene (PTFE), used in filtration processes, were also investigated as models for hydrophobic materials [6] characterized by high and low ionic conductivity, respectively. Both non-zero gap and zero gap atmospheric pressure laboratory scale electrolysis cells, operating at room temperature, were developed and a comparative study of their advantages and disadvantages







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Fig. 1. Lab-scale electrolysis set-up: a) non zero gap, and b) zero gap four-electrode two-compartment electrochemical cell, with the indicated position of the poly(vinyl chloride) (PVC) capillary serving as a holder for a quadrupole mass peftrometer (QMS) detection capoillary. Sense and reference electrodes are marked as SE and RE, respectively.

for the lab scale electrochemical characterization of gas separator materials was undertaken.

2. Experimental

2.1. Materials and Solutions

Asbestos samples used in this study were cut from a typical separator for alkaline electrolyzers (chrysotile, $Mg_3Si_2O_5(OH)_4$). Polyphenylene sulphide (PPS) type 306P41 5/5, with an area weight of 550 [g m⁻²] and air permeability of 160 [l dm⁻² min⁻¹] at 200 Pa, has been supplied by Heimbach Filtration GmbH. Additionally, the properties of PPS impregnated with RASTEX® expanded polyte-trafluoroethylene (PTFE) were also investigated.

Thickness of the PPS separator was 2 mm, asbestos separator 4 mm and PPS with PTFE 1.8 mm, while all separators had a diameter of 20 mm. During the measurements in the zero gap cell asbestos separators were pressed until they reached the thickness of 2 mm. The differences in the separators' thickness were taken into account for the calculation of the conductivity (paragraph 3.1, Equation 3). The separators surface area exposed to the electrolyte in a half-cell was 2.54 cm², due to the O-rings mounted on their both sides and

covering the edges of the separator. All the samples were in a dry condition initially, followed by forced soaking of the 25 wt. % KOH using an air-pump device, and were stored in the same electrolyte before the experiments.

Prior to experiments in the non-zero gap cell the samples were immersed in 25 wt. % KOH solution for at short term (less than one week) and long term (three months). The measurements after long term immersion of the separators were only undertaken with the non-zero gap cell in order to provide an indication on the influence of longer exposure to the strongly alkaline environment, present in the alkaline electrolysis, on the separators' critical parameters, such as ionic conductivity and oxygen permeability. Prior to the experiments in the zero gap cell the samples were immersed in the electrolyte for a short term only (less than one week).

The non-zero gap cell (Fig. 1a) is a two compartment 4-electrode cell where two Ni disks (20 mm diameter, 2 mm thickness, Alfa Aesar[®], 99.95% purity), anode (working electrode, oxygen evolution) and cathode (counter electrode, hydrogen evolution), are placed far from the separator installed in the middle of the cell. Two lead/lead fluoride micro electrodes Pb/PbF₂ filled with 0,5 M NaF (-0.530 V vs. Ag/AgCl at 25 °C) [7] served as a sense and a reference electrode. Prior to experiments the Ni disk electrodes were

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