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BUILD UP OF A PILOT- AND DEMONSTRATION ALKALINE ELEC-TROLYSER FOR TESTING OF ADVANCED DIAPHRAGMS

Schlussbericht

Ausgearbeitet durch

Dr. Ulrich Vogt, EMPA
ulrich.vogt@empa.ch

Prof. Andreas Züttel, EMPA
andreas.zuettel@empa.ch

Dr. Ivo Trajkovic, EMPA
ivo.trajkovic@empa.ch

MSc. Michal Gorbar, EMPA
michal.gorbar@empa.ch

E. Burkhalter, IHT
eb@iht.ch

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Mühlestrasse 4, CH-3063 Ittigen

Postadresse: CH-3003 Bern

Tel. +41 31 322 56 11, Fax +41 31 323 25 00

www.bfe.admin.ch

BFE-Bereichsleiter: Dr. Stefan Oberholzer (stefan.oberholzer@bfe.admin.ch)

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Abstract

The objectives of the project are the development of a fully automated pilot scale electrolyser at IHT for testing and characterizing new types of diaphragms/membranes for high pressure, zero gap alkaline electrolyser. At EMPA, membranes of new alternative materials are produced and tested on laboratory scale concerning electrochemistry and stability.

Industrie Haute Technologie (IHT), Monthey, CH, produces alkaline electrolysers with a capacity for hydrogen generation of 760 Nm^3/h H_2, an electrical consumption of 4.3 kWh/Nm^3 and a total efficiency of 82%. Nowadays, IHT is facing the imminent necessity to replace the asbestos diaphragm used traditionally in their electrolysers with a diaphragm made of advanced and environmentally friendly material.

The new materials has to fulfill multiple demands, such as good gas separation, fast evacuation of the bubbles from the surface (low sticking coefficient), good ionic conductivity and low cell overpotential, combined with a high chemical stability in 25 wt. % KOH solution at 85°C, mechanical strength as well as economic and ecological acceptance. The new developed diaphragms are based on minerals, ceramics, polymers and composites thereof.

While at EMPA the new materials has been developed and tested in laboratory scale and ambient conditions (room temperature, ambient pressure), IHT was building up the pilot plant electrolyser for testing the new membranes under industrial conditions at 80°C and 30 bar.

Einleitung / Projektziele

The development of clean, sustainable and cost-competitive hydrogen is the key to a viable future hydrogen economy [1, 2]. The leader in producing high pressure zero gap alkaline electrolysers, IHT, CH is facing the imminent necessity to replace the asbestos diaphragm used traditionally in their electrolysers since the 1950s, with a separator made of advanced environmentally friendly and non-insalubrious material [3]. While diaphragm respectively membrane materials has been already developed and produced at EMPA in the laboratory scale (20-50 mm diameter) during the CTI project NMAE2, (KTI-Projekt Nr. 8574.2 PFIW-IW), the goal of the following up P+D project is to building up a pilot plant electrolyser at IHT, as well as producing and testing new membranes with 130 mm in diameter under semi-industrial conditions. This is a precondition for a following up-scaling of the membranes to the industrial size of 1.6 m in diameter.

Also, there is a requirement from the market for electrolysers in the power range of 1 – 5 kW which is the same dimension as the pilot plant electrolyser. Nowadays this range is covered by PEM electrolysers with lower efficiency and higher investment costs than alkaline electrolysis.

Kurzbeschrieb des Projekts

The separator in electrochemical reactors can be referred to as a diaphragm or a membrane [13]. Permeable membranes which permit the bulk flow of liquid through their structure and are thus non-selective regarding transport of ions or neutral molecules are in electrochemical processes referred to as diaphragms. Semi-permeable membranes have the property of ion-selectivity and are referred to as simply membranes [14].

A diaphragm should fulfill multiple requirements, such as: good gas separation and fast evacuation of the bubbles from the surface (low sticking coefficient), increased ionic conductivity and chemical stability in highly concentrated KOH solution (above 25 wt. %) at 85°C. Moreover, the mechanical strength is required taking into account that industrial diaphragms have 1.6 m in diameter and are exposed to elevated pressure. Further on, the material should be cost effective, non toxic, and provide a safe operation over at least 10 to 20 years. The permeability and ion-conductivity of diaphragms used in alkaline electrolysis depend on the materials pore structure. An open pore structure should provide holding a sufficient amount of electrolyte in a diaphragm.

The porosity of the diaphragm influences the ion conduction and the gas purity and is therefore a crucial parameter. Asbestos-chrysotile diaphragms with a porosity of ca. 40% (Fig. 1) [4] are chemically stable in the caustic electrolyte and exhibit sufficient ion conduction.

The group II, IV and VIII metal oxides (e.g. NiO, ZrO_2, MgO, TiO_2) have been investigated as diaphragm materials by Renaud et al. [5], Vogt et al. [6] and Wendt et al. [7]. However, fabricating thin sintered sheets with large diameter remains a challenge due to the brittleness of metal oxide materials after sintering. Organic polymers, such as polysulfone, polyphenylene sulfide and fluorinated polymers as matrix material in combination with oxides allow the manufacturing of composite diaphragms [8]. Polymers are hydrophobic, therefore gas bubbles tend to accumulate at the diaphragm-electrolyte interface [7]. Gas bubbles reduce the efficiency of electrolysis because of the reduction of the membrane cross section and thus the ion conduction [9].

An important prerequisite for the development of alternative material concepts is the fundamental understanding of the correlation between microstructure and cell performance. A first investigation on porosity effects vs. ionic conductivity of several alternative materials, based on organic and inorganic compounds has been carried out at EMPA.

Different alternative materials have been analyzed with the Electra electrolysis cell, developed at EMPA, which operates at atmospheric pressure and room temperature and thus not under real operating conditions like industrial cells. The lab scale cell permits to compare between the properties of asbestos and new alternative materials by operating under matchable conditions.

Materials that are most close to the asbestos in terms of cell voltage and gas purities will then be tested in the pilot plant facility working at industrial operating conditions, meaning 85°C operating temperature, 30 bar operating pressure and 25% electrolyte (KOH) concentration.

Durchgeführte Arbeiten und erreichte Ergebnisse

In order to attain the objectives related to diaphragm material development, different materials has been taken in consideration like minerals, ceramics and the combination with polymers.

The chosen materials has been investigated and compared to the commercial asbestos-chrysotile diaphragms. One of the issues was to improve ceramic materials concerning mechanical strength by structural reinforcement, keeping the structure partly flexible and mechanically stable.

Commercial diaphragms

The asbestos chrysotile diaphragm used from IHT, was chosen as a reference sample due to the chemical stability in 25 wt% KOH at 85°C and 30 bars; sufficient wettability and ions conduction. With Asbestos membranes, the purities of produced hydrogen and oxygen during electrolysis reach 99.99% and 99.96%, respectively in industrial scale electrolysers.

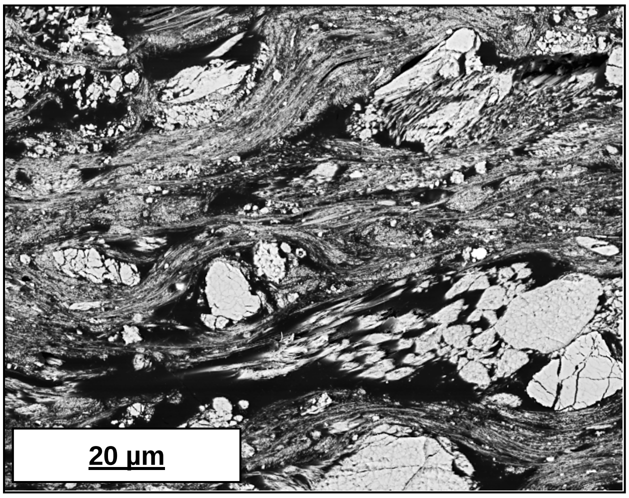

Figure 1 Asbestos diaphragm embedded into organic resin to keep a thickness of 2,5 mm in conventional electrolysers [4].

Chrysotile, whose chemical formula is $Mg_3Si_2O_5(OH)_4$, is a natural, tri-octahedral, layered silicate mineral which belongs to the serpentine group and is classified as asbestos due to its fibrous nature [10]. A crystallographic misfit between layers of SiO_4-tetrahedra (T) and $Mg(OH)_2$-octahedra (O) causes bending of the TO-stacks of the chrysotile structure forming closed, hollow, and nano-sized cylinders with the T-layer on the inner side of the cylinder [10][11][12]. These nanotabular fibers show high length/diameter ratios and build bundles, which are sufficiently flexible and stable to be processed as cloths, papers or boards for the use as gas separation diaphragms in alkaline electrolysis (Fig. 1).

Commercial alumina oxide ceramic matrix composites (CMCs) of AVA-Z-ICS (Pritzkow, Germany) have been investigated in a first round, but neglected due to insufficient stability in KOH. The chemical stability of the CMC was determined by leaching it in 25 wt%, 30 wt% and 50 wt% KOH solutions for 1150 hours at 85°C. The samples have been determined by gravimetric method and XRD, the density was investigated by the Archimedes method with adequate porosity calculations. Scanning electron microscopy (SEM) was performed for optical evaluations. Tests concerning the chemical stability of CMC based diaphragms in KOH solution show a linear decrease in weight for increasing KOH molarity. After 1150 hours of leaching at 85°C the weight loss was 5.55% ± 0.3% for 25 wt.% KOH, 6.15% ± 0.33% for 30 wt.% KOH and 7.23% ± 0.37% for 50 wt.% KOH. The X-ray diffraction analysis did not show any changes in the crystallographic structure.

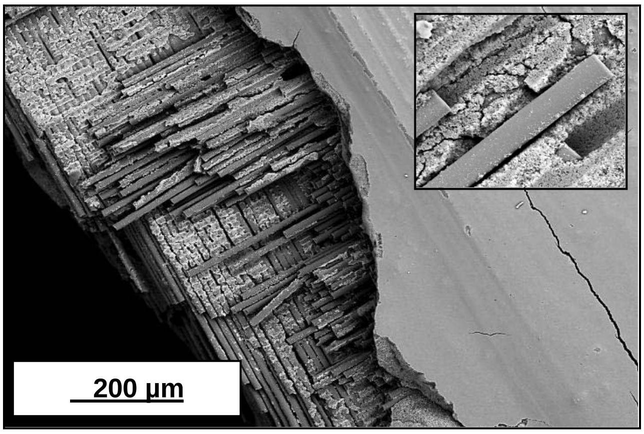

Figure 2 Scanning electron microscopy image of alumina based CMCs of AVA-Z-ICS (Pritzkow, Germany); α-Al_2O_3 fibers stabilize the dense composite matrix of ZrO_2-Al_2O_3.

Mineral and ceramic based composite diaphragms

The polymeric matrix material (e.g. PPS, polyphenylene sulphide) was simply impregnated by viscous polymer/solvent/inorganic powder slurry, produced by a milling and mixing process. As a liquid medium, the polar aprotic solvents are used (e.g. DMF-dimethylformamide, DMA-dimethylacetamide, NMP-1-methyl-2-pyrrolidone) to dissolve organic binder of PSU-polysulfone. Inorganic fillers (ZrO_2, $BaTiO_3$, $BaSO_4$, Olivine, Wolastonite, Baryte) improve wettable properties and thus keep the sticking coefficient low. The slurry consists of 5 parts of inorganic filler, 2 parts of PSU (UDEL P-3500, Solvay) and 48 parts of N-Methyl-2-pyrollidone (Sigma-Aldrich). As grinding media 200 g zirconium dioxide-balls with a diameter of 5 mm were used.The binding effect between polymer/particles and polymer/matrix material is occurred by a phase inversion process, when impregnated (infiltrated) diaphragms are immersed into a non-solvent bath (Fig. 3).

a: **b:** **c:**

Figure 3 Basic concept of diaphragms preparation (from left): a: polyphenylene sulphide fabric PPS; b: immersed in polymer/solvent/inorganic powder slurry; c: coagulation of the impregnated diaphragm in a non-solvent bath.

The open-porous inorganic/organic structure is formed due to diffusion of non-solvent molecules into the polymeric organic/inorganic matter and subsequently, the solvent is washed out. Various porosities can be achieved by changing the ratio between initial compounds and character of the non-solvent bath. The process guarantees the fixing of inorganic particles in polymeric matter. However, further structural investigation seemed to be difficult mainly due to the fact, that all impregnated diaphragms need to be kept in the wet stage. Environmental scanning electron microscope was used to investigate the prepared diaphragms in the wet stage. By changing the pressure conditions in the microscope chamber (decreasing the pressure), we experienced the drying phenomena of the diaphragms.

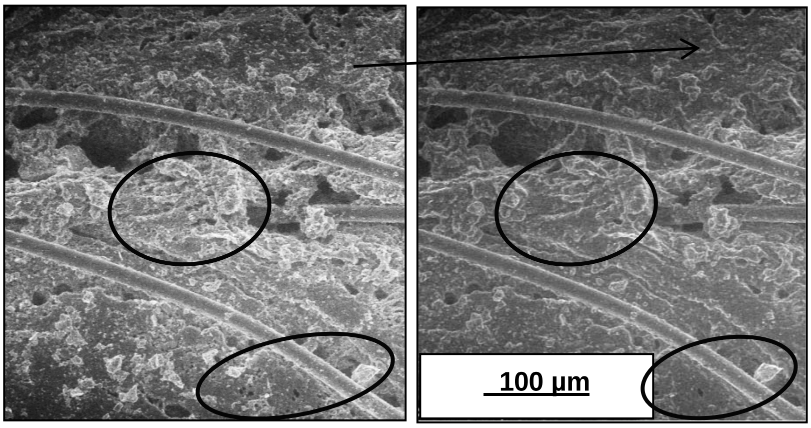

Figure 4 Environmental scanning electron microscope imaging gives the possibility to qualitatively indicate the drying effect on the diaphragm microstructure. The analysis revealed that upon removal of water, structural deformation occurs as a result of pores packing within the matrix body.

The method Raman mapping of the diaphragms was investigated for a better understanding of segregation effects between individual compounds within the matrix. The distribution of the ratio of olivine and polysulfone in a diaphragm is shown by contour plots in the figures 5 and 6. In this case the amount of polysulfone is high close to the fibres, while the concentration of olivine is high in the space in between them. The effect is most prominent in diaphragms prepared from a polyphenylene sulphide fabric, which were infiltrated first with pure olivine and then subsequently impregnated with polysulfone coated olivine (Fig. 6). The segregation is caused by the different strengths of intermolecular interaction between the components of the diaphragms. The polymers interact via van-der-Waals-forces and hydrogen bonds, while olivine binds only weakly to the polymers. Due to Coulomb forces the mineral agglomerates inside the structure in small particles. Completely coated olivine sticks to the fibre, while less coated particles agglomerate inside the fabric. Thus near to the polyphenylene sulphide fibres a higher concentration of polysulfone compared to the olivine is found. The preferred binding of the polysulfone-olivine to the polyphenylene sulphide matrix is reduced by the infiltration step leading to certain instabilities mainly during the phase inversion process when inorganic filler is washed out from the structure. A repeated impregnation leads to the most stable samples, even though a minor segregation is achieved. However, the amount of inorganic filler is then reduced in the inner part of the polyphenylene matrix. Therefore the diaphragms must be prepared in the way of thicker felts. The required diaphragm thickness of 2.5 – 3 mm for the electrolyser cell can be adjusted by mechanical pressing.

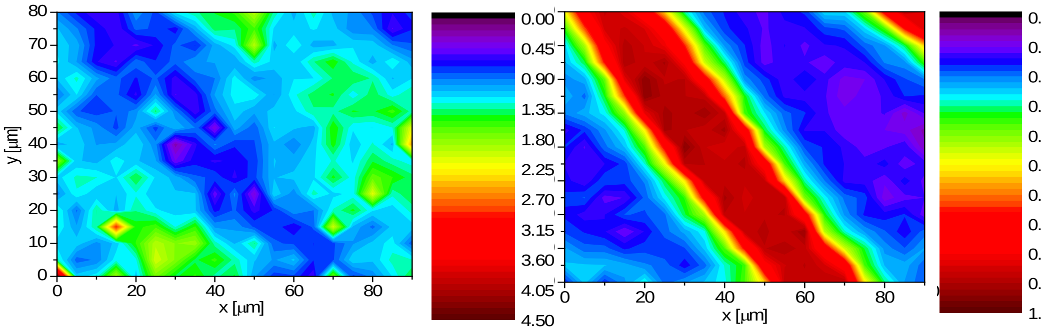

Figure 5 Raman mapping of the 2-times impregnated composite diaphragm; left: contour plot of ratio between inorganic filler (olivine) and organic binder (polysulfone PSU); right: contour plot of PPS polyphenylene sulphide fibers distribution within the diaphragm body.

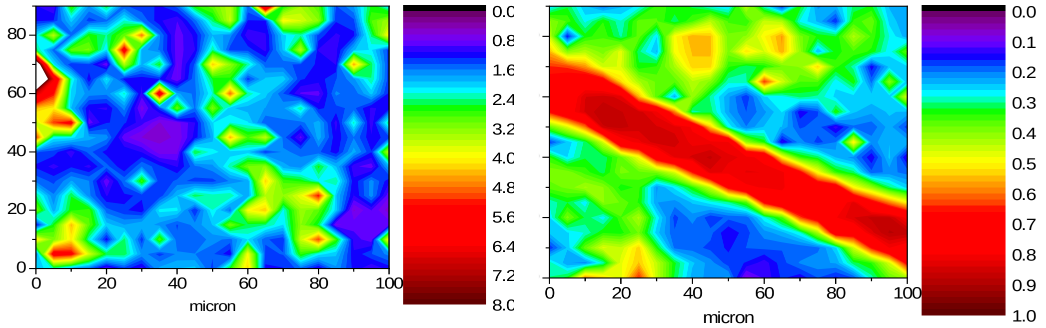

Figure 6 Raman mapping of the one-time infiltrated and then impregnated composite diaphragm; left: contour plot of the ratio between inorganic filler (olivine) and organic binder (polysulfone PSU); right: contour plot of the PPS polyphenylene sulphide fibers distribution within the diaphragm body.

Electrochemical set ups and proceeding

An **experimental setup** with a small-scale electrochemical cell (Figure 8) has been successfully built up and used to electrochemically characterize the newly produced $BaTiO_3$, olivine, ZrO_2, and $BaSO_4$ diaphragms with 20 mm diameter (labscale). The ion conductivity through these diaphragms turns out to be in the range of 0.2 – 0.32 S/cm which is significantly higher than for asbestos with 0.12 S/cm. Their porosities (ratio between the volume seized by all pores and the total diaphragm volume) were determined by Helium pycnometry, varying in the range of 65-71 % somewhat higher than for asbestos which was determined to be 51.9 %. Conclusively, the ion conductivity through the novel diaphragms shows values which are higher than the values for asbestos. In a further step, their gas separability will be measured to complete the comparison with asbestos (Fig.7).

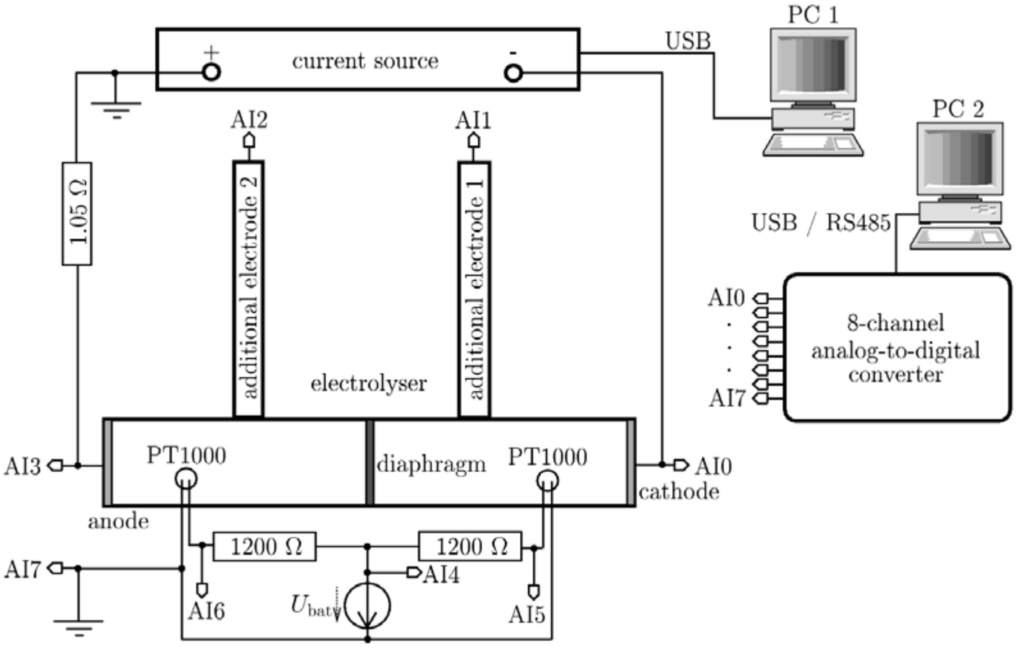

Figure 7 The experimental setup with a small-scale electrolyser for Ø 20 mm diaphragms.

For electrolytic experiments a lab electrolyser has been build up at EMPA for ambient conditions (Fig. 8). Experiments are performed at 25°C and ambient pressure in a 2-compartment 2-electrode cell made of polysulfone with electrodes based on Raney Ni meshes and 25 wt.% KOH as electrolyte solution. The system allows us to regulate the speed of circulating electrolyte and so control the bubble evolution process on both sides. The current density in the range 100 – 500 $mA*cm^{-2}$ can be set up in three possible ways in time dependence: i.) constant value, ii.) linearly increasing and iii.) stepwise increasing.

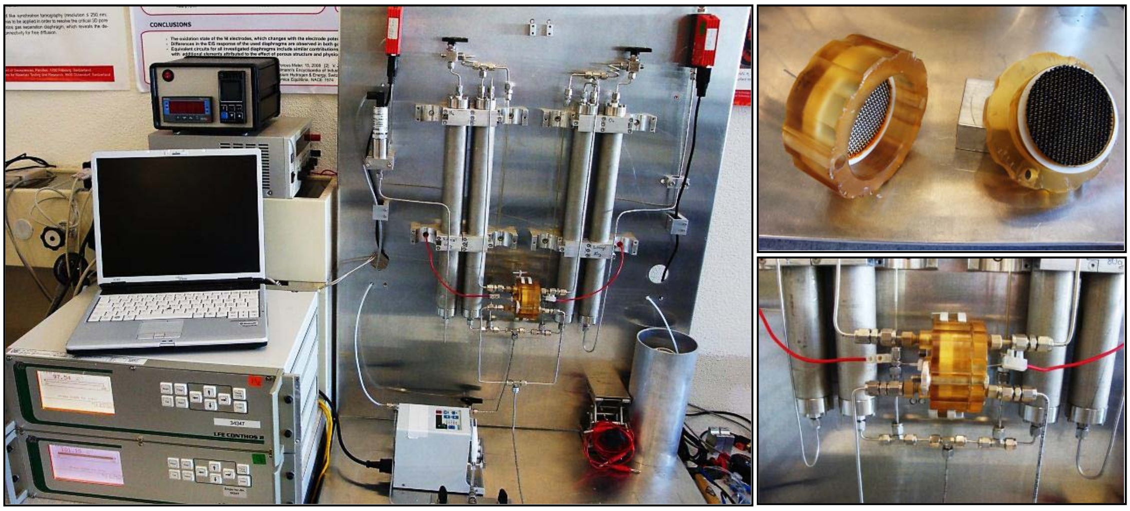

Figure 8 Laboratory electrolysis cell made of polysulfone (transparent) with an inner Ø of 50 mm of, Ni Raney electrodes, working at ambient condition.

Construction, build up and installation of a pilot plant electrolyser (IHT)

Over the period of the project, a fully automated pilot-scale electrolyser for a membrane diameter of 130 mm was built up at IHT. Therewith it is possible to test the stack efficiency and durability under real conditions using components (electrodes, membranes) made of newly developed advanced materials. The pilot plant is built up in a modular way which offers manifold possibilities for testing of different cells, resp. membranes and electrodes. The new pilot plant is compact, cost effective, safe for operation and dynamic regarding H_2 output and thus power consumption (Fig. 9).

First tests has been carried out on samples of the following composition, prepared at EMPA:

$BaSO_4$ – 4PSF/NMP, MATRIX => PPS (polyphenylene sulphide) felt, < 4mm thickness
COATING => 4wt.% PSF/NMP and $BaSO_4$ Sigma Aldrich
Olivine – 4PSF/NMP, MATRIX => PPS (polyphenylene sulphide) felt, < 4mm thickness
COATING => 4wt.% PSF/NMP and Olivine
$BaTiO_3$ – 4PSF/NMP, MATRIX => PPS (polyphenylene sulphide) felt, < 4mm thickness
COATING => 4wt.% PSF/NMP and $BaTiO_3$ Sigma Aldrich
ZrO_2 – 4PSF/NMP, MATRIX => PPS (polyphenylene sulphide) felt, < 4mm thickness
COATING => 4wt.% PSF/NMP and ZrO_2 TZ-3Y Tosoh

The results of the first tests will be analysed and compared to conventional asbestos membranes as well as commercial Zirfon membranes from VITO/AGFA, based on ZrO_2 powder and polysulfone.

Figure 9 Pilot plant build up at IHT during 2011

Nationale / internationale Zusammenarbeit

National cooperation in the project exits with the company IHT. While Empa is developing and testing new membrane materials, IHT was responsible for the construction of the pilot plant reactor and measurements of the newly developed mambranes.

International cooperation has started on November 2011 within the FP7 project ELYGRID (“Improvement of Integrated High Pressure Alkaline Electrolysers for Electricity/H2 Production from Renewable Energy to Balance the Grid” Grant Agreement No: 278824), as well as the infrastructure project H_2FC, (Integrating European Infrastructure to support science and development of Hydrogen- and Fuel Cell Technologies toward European Strategy for Sustainable, competitive and Secure Energy, Proposal Nr. 284522) where the department Hydrogen&Energy is involved due to the competences build up during the CTI and BFE-Swisselectric activities.

Bewertung 2011 und Ausblick

The preparation of diaphragms with diameters of 20 mm for electrochemical characterization, 50 mm for laboratory electrolysis experiments and 130 mm for the prototype pilot plant could be demonstrated at EMPA. The electrochemical characterization methods for diaphragm tests at EMPA will further be improved for a semi-automatic operation and thus better and more reproducible results.

The pilot plant at IHT has been finished and used for testing first new types of membranes under realistic conditions at 80°C and 30 bar. The results will be evaluated and interpreted during in beginning 2012.

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Michal Gorbar, Ulrich F. Vogt, Ivo Trajkovic, Daniel Wiedenmann, Andreas Züttel, Development of Advanced Diaphragms for Alkaline Electrolysers, Abt.138 EMPA • Ernest Burkhalter, IHT SA, (Swiss Electric Research Award 2011, Technopark Zurich, Switzerland) (Poster)

M. Gorbar, U. F. Vogt, D. Wiedenmann, J. Stojadinović, B. Fumey, A. Züttel, Advanced gas separation diaphragms for alkaline electrolysis, (27th Symposium, Electromobility Day, PSI Villingen, 11. 05. 2011 Switzerland) (Poster)

U. F. Vogt, M. Gorbar, D. Wiedenmann, J. Stojadinović, V. Zakaznova-Herzog, A. Züttel, Development of Advanced Gas Separation Diaphragms for Alkaline Electrolysis, (Workshop on "Capture and conversion of CO2 into sustanable hydrocarbon fuels", in Roskilde, Denmark, 14. - 15.04.2011 Technical University of Denmark, 2011) (Poster)

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