Executive Summary:

In the context of global warming and climate change concerns, the proportion of hydrogen produced by electrolysis is expected to increase rapidly, using the electricity from renewable sources. At present however, a barrier to its use is the economy, and new technologies must therefore be developed. Compared to the conventional alkaline electrolyte electrolyser, the polymer electrolyte membrane (PEM) electrolyser can operate at high current densities and pressure with compact design. The main challenges for PEM electrolysers are high capital cost of key materials, components and the overall system as well as insufficient long-term durability. The strategic development of the WELTEMP project is an elevated operating temperature of the PEM electrolyser. In this way the energy efficiency will be significantly improved because of enhanced electrode kinetics, the decreased thermodynamic energy requirement, and the possible integration of the heat recovery. The elevated temperature requires either that the water electrolysis is carried out on steam, or that the working pressure is raised to keep the water liquid.

Key issues to achieve this strategic target are breakthroughs of fundamental materials developments, including catalysts, membranes, current collectors, bipolar plates and other construction materials. Therefore the activities of WELTEMP was organised in five workpackages: Electrocatalytic materials, Polymeric membranes, Metallic construction materials, preparation of membrane-electrode assemblies (MEAs), and making a stack of cells based on the new materials. Within this project structure Weltemp has adressed materials and technologies within three different concepts of PEM electrolysers while attempting to elevate the working temparature: 1) Steam electrolysis at ambient or low pressure on the basis of proton conducting (acidic) membrane electrolytes, 2) Electrolysis of pressurized water on the basis of proton conducting (acidic) membrane electrolytes. 3) Electrolysis of pressurized water using alkaline polymeric electrolytes.

For use with alkaline membranes new non-noble metal based (i.e. low cost!) catalysts were successfully developed. For use with acidic membranes a new preparation procedure for usual IrO2 was introduced in order to improve the durability.

The activities within proton conducting (acidic) membranes was based on modifications of two types of materials: 1) phosphoric acid doped polybenzimidazole (PBI) membranes, and 2) perfluorinated sulfonated (PFSA) membranes. The PFSA membrnanes were the most successful for two main reasons: (i) negative impact of the phosphoric acid on the anode catalyst activity and (ii) by the strongly limited stability of the PBI based membrane in the water electrolysis cell. It was demonstrated that steam electrolysis (ambient pressure and 120-130oC) can be carried out using PFSA type membranes, but in this case it is necessary to dope them with phosphoric acid in order to maintain their protonic conductivity.

In addition, new ion conducting alkaline membrane materials were introduced for testing.

It was found that tantalum coated stainless steel could fulfill the very high demands to corrosion resistance under acidic conditions due to the elevated temperature. Such material was prepared by high temperature chemical vapor deposition.

A potential of long time durability was demonstrated for alkaline MEAs, but the performance was not high. For acidic systems, the highest performances were obtained for systems pressurized to 3-7 bar, and at temperatures 120-130oC. Here, voltages of 1.65 V at 1.0 A/cm2 and 1.85 V at 2.0 A/cm2 were observed.

Project Context and Objectives:

The WELTEMP project funded by the European Union was a collaborative project under the Seventh Framework Programme (FP7). The project involved partners from five European countries (Denmark, Norway, Czech Republic, Switzerland and Italy), and was running from 1.1. 2008 to 30.04.2011.

Water electrolysis offers a practical way of hydrogen production in association with renewable energy sources. The barrier to its use is the economy, and new technologies must therefore be developed. Compared to the conventional alkaline electrolyte electrolyser, the polymer electrolyte membrane (PEM) electrolyser can operate at high current densities and pressure with compact design. The main challenges for PEM electrolysers are high capital cost of key materials, components and the overall system as well as insufficient long-term durability. The strategic development of the WELTEMP project is an elevated operating temperature of the PEM electrolyser. In this way the energy efficiency will be significantly improved because of the decreased thermodynamic energy requirement, enhanced electrode kinetics, and the possible integration of the heat recovery. The elevated temperature requires either that the water electrolysis is carried out on steam, or that the working pressure must be raised.

Key issues to achieve this strategic target are breakthroughs of fundamental materials developments, including catalysts, membranes, current collectors, bipolar plates and other construction materials. The WELTEMP activities included development of active and stable anodic catalysts based on mixed metal oxides, temperature-resistant PEM based on composite PFSA, sulfonated aromatic and/or acid-base cross-linked polymers, and highly conducting and corrosion-resistant tantalum thin surface coatings as current collectors and bipolar plates. As an alternative, the possibility to make an alkaline PEM electrolyser was also examined, i.e. to use an anion conducting polymeric electrolyte. In this case, the need for noble elements as electrocatalysts will be strongly diminished. On the other hand, the difficulty is to develop a polymeric membrane, which is sufficiently stable, mechanically as well as chemically, at elevated temperatures.

Project structure:

Overview of Work Packages and Tasks:

WP 0 Management

Task 0.1 Internal management

Task 0.2 External coordination and communication

WP 1 Catalysts

Task 1.1. Preparation of noblemetal catalysts

Task 1.2. Novel catalysts (non-noble metals)

Task 1.3 Characterisations of catalysts

WP 2 Membranes

Task 2.1. Modified PFSA membranes

Task 2.2 Composite membranes

Task 2.3 Acid-base polymer membranes

Task 2.4 Anion exchange membranes

WP3 Construction materials

Task 3.1 Current collectors

Task 3.2 Materials for bipolar plates

Task 3.3 Characterisations of materials

WP4 MEA fabrication

Task 4.1 Fabrication of MEA´s

Task 4.2 electrolyser test rig

Task 4.3 Evaluation of MEA´s

WP5 Prototype stack

Task 5.1 Design of electrolysers

Task 5.2 Prototype electrolyser

Task 5.3 Testing of prototype electrolyser

Task 5.4 System competitiveness

Project objectives:

The scientific and technological objectives of the WELTEMP include:

(1). Development of temperature-resistant polymer electrolyte membranes with

- Operational temperatures from 120 to 200°C

- Ionic conductivity of 0.05 - 0.10 S/cm
- Good chemical (oxidative) stability and mechanical flexibility
- Durability over 5,000 hours

(2). Active and stable electrocatalysts with aims of

- Anodic overpotential for oxygen evolution of less than 350 mV at 1 A/cm² with a noble metal loadings of < 2 mg/cm²
- Cathodic overpotential for hydrogen evolution of 60 mV at 1 A/cm² with a noble metal loadings of < 0.2 mg/cm²
- With performance loss < 20 mV/h during a period of 5000 h´

(3). Preparation of membrane-electrode assemblies (MEAs) with targets of

- Development of an MEA fabrication method
- Fabrication of MEAs of 10 cm diameter size
- Single cell performance of 1.55 V at 1.0 A/cm²
- Pressurizable up to 30 bars or more
- Operational temperatures 120-200°C

(4). Tantalum coated current collectors based on titanium with

- Excellent corrosion resistance at temperatures up to 200°C
- Specific electronic resistance of less than 10 mOhm cm
- Prototype production and low material and production cost

(5). Tantalum coated bipolar plates based on titanium or alternative metals with

- Specific electronic resistance of less than 0.1-1.0 mOhm cm
- Heat conductivity (> 10 Wm-1K-1)
- Little gas permeability (< 10-7 mBarL s-1cm-2)
- Good flexibility and suitable for gas-tight sealings

(6). Design and construction of a 1 kW prototype electrolyser

- Flexible modular design of 5 cells with active MEA area of 78 cm2.
- Selection of sealing materials and development of sealing concepts
- Low parasitic energy consumption

(7). Testing of the 1 kW prototype electrolyser

- Operational at temperatures above 120°C
- Operational at pressures from 20 bars to 70 bars.
- Hydrogen production of 320 NL/h
- Single cell efficiency higher than 80 % on an LHV basis
- Non-energy production cost of 1 EUR/kg of hydrogen, if mass produced

Project Results:

Main Achievements (Results/foregrounds) of the project

(Figure captions are given in the text, Figures including captions are found as an attachment)

WP 1. Catalysts

1. Preparation and characterisation of noble-metal based catalysts

The work relied initially on iridium oxides prepared by hydrolysis or polyol synthesis techniques as described by for example Lervik (I. A. Lervik M. Tsypkin, L.-E. Owe, S. Sunde, "Electronic structure versus electrocatalytic activity of iridium oxide", J. Electroanal. Chem. 645 (2010) 135) . In addition a thermolytic technique for producing iridium oxide was developed. Essentially, recrystallised iridic acid was fired at high temperature and under oxygen. XRD-patterns were consistent with the rutile structure, and indicated a crystallite size of 3 through 6 nm.

A number of different additives to iridium oxides, like Ta and Mn, was tested in order to improve the catalyst activity and stability. The initial performance of mixed oxide catalysts is better than the initial performance of thermally prepared powder of pure iridium oxide, c. f. Fig. 1 below. The same was observed for iridium oxide prepared by the hydrolysis method. The performance of all catalysts but the thermally produced powder decreases very fast during the first 20-30 hours, however. At the end of this period the activity of the thermal powder is getting the best. For long term operation of the electrolyser we therefore chose to continue the development of the thermally prepared iridium oxide.

In addition, surface area as measured electrochemically by cyclic voltammetry revealed a much more open structure for the thermolytically produced catalysts than those produced by hydrolysis. From the results we conclude that in case of thermal oxide almost all surface can participate in oxygen evolution reaction and the noble metal utilization is very high.

Fig. 1. Normalised current density at constant potential for various iridium oxides as indicated in the legend. The measurements were conducted in 0.5M phosphoric acid at ambient conditions.

A correlation between particle size calculated from outer surface (using approximation that all particles have the same size and spherical shape) and crystallite size estimated from XRD modeling is presented in Fig. 2. These two parameters are plotted for the same batch of the catalyst there. The correlation is the most pronounced in a range of sizes above 3 nm, but below this limit the measurements of sizes from diffraction data has large error due to the method limitation for particles below 2-3 nm.

Fig. 2. Comparison between particle size measured by XRD and by electrochemical method

Stability of the catalysts as a function of particle size is displayed in Fig. 3, normalised by voltammetric charge. A clear effect of particle size is evident; the smaller the particles the larger the degradation rate.

Catalytic inks prepared from Nafion solutions and the catalysts, sprayed onto Ta-coated felt with an airbrush, which was finally dryed and heated. The MEA testing was performed in a custom built multi-fuel PEM fuel cell test station, designed for temperatures and pressures up to 200 °C and 16 bar, and with a 5 cm2 golden-plated stainless steel cell with parallel flow field pattern (in house made). Cell potential and current were controlled by an electronic power supply.

Fig. 3. Specific electrochemical activity of the prepared materials. The current was normalized by outer charge

Fig. 4. MEA performance measured in a single cell with Nafion 115, saturated by ZrP. Cathode electrocatalyst - Pt/C (20%), anode catalyst - prepared IrO2. Cell temperature - 110oC, steam conditions.

Polarisation curves for two different particle sizes are shown in Fig. 4. As is apparent from the figure, the smaller the particels, the higher the activity. This clearly demonstrates the trade-off between activity and stability in terms of particle-size.
The effect of phosphates are displayed in Fig. 5. We also performed extensive measurements on electrolyte effects on catlyst produced by hydrolysis, including polarisation curves in perchloric acids and as a function of temperature. The general conclusion is that phosphoric acid has a rather detrimental effect on the performance of the catalyst.

Fig. 5. Dependence of electrolyte on catalyst performance. The dependences was measured in 0.5 M acids. Ambient conditions, electrocatalyst with grain size 4.5 nm.

2. Novel catalysts based on non-noble metals

Oxygen Evolution Reaction (OER) catalyst:

Initially, a series of NiCo2O4 based catalysts prepared. They were synthesized by thermal decomposition using nitrate salts (method adapted from J. F. Marco et al., J. Mater. Chem. 2001, 11, 3087-3093). The catalyst thus obtained had very good activity when prepared in small batch sizes (up to 120 g). However, at larger batch sizes the activity was poor. This was shown to be caused by low electronic conductivity due to impurities.

A major objective was then to obtain an alternative catalyst that could be prepared on a large scale (250 g) with good reproducibility in terms of activity and performance in an electrolysis cell. Thus another Co containing mixed oxide type material was prepared. The preparation method was similar to that utilised for the Ni based material but was much less complicated in terms of time and conditions. Additionally, the removal of Ni salts from the procedure is advantageous in terms of health and safety.

The material was characterised by XRD and ICP-OES. All major peaks in a typical XRD can be assigned to the expected phases. In addition the composition of the material was also confirmed by elemental analysis.

A cyclic voltammetric scan for the OER catalyst is shown in Fig. 6.

Fig. 6. Oxygen evolution activity determined by RDE experiments of four production batches at 250 g scale.

The reproducibility in the activity from batch to batch is excellent and the material can be produced on a 250 g scale. This material was incorporated into anode electrodes and the performance was studied in test electrolysis cells (see below).

Hydrogen Evolution Reaction (HER) catalyst:

Also in the case of the HER catalyst for alkaline conditions, a non noble metal (or non PGM = non platinum group) catalyst material was prepared. This was a supported type of catalyst material, in which preparation procedure involved a wet chemistry procedure, followed by drying, ball milling, calcination and finally reduction under hydrogen.

The results on the kinetic activity of this new HER catalyst compared with a Pd based catalyst (3020) and 10% Pt/C are shown in Figure 7. The new catalyst shows the same over-potential for the hydrogen evolution reaction as the Acta benchmark catalyst 3020 (with 5 wt% Pd) and has a 120 mV over-potential increase when compared to the commercial catalyst 10 wt% Pt/C at 20 mA/mgcat. The performance of this non PGM HER catalyst in water electrolysis test cells is described in the next section.

Fig. 7. HER cyclic voltammetry (RDE) data for the new non PGM HER catalyst, the Pd catalyst 3020 and a commercial 10 wt% Pt catalyst.

Water electrolysis performance of ACTA non PGM catalysts in test cell

Fig. 8 shows a comparison of the performance of a simple nickel foam anode with one of the new OER catalysts on the anode, using the same cathode (Pt on Ni). The Catalyst based anode performs better than simple nickel foam over the whole current density range.

Fig. 8. Plots of applied cell voltage (without IR correction) as a function of water electrolysis current density comparing the performance of nickel foam current collectors with and without new OER catalyst.

In conclusion, both non PGM anode and cathode catalysts developed in ACTA for the alkaline electrolysis cell were fully characterised and produced at the 250 g scale. Performance in electrolyser cells at 80 °C is as good if not better than PGM based cells (500 mA/cm2 at 1.7 V).

WP 2. Membranes

1. Modified PFSA membranes

Stability of the commercial Nafion membranes

Perfluorinated sulphonated materials represent state of the art in the polymer electrolytes for the acidic version of the water electrolysis process. They are characterized by the high ionic conductivity, excellent chemical and mechanical stability and last but not least by good compatibility with the anode and cathode catalyst. This makes them potentially favorable option for the application in the

PEM water electrolysis. The main problem in the desired application is strong dependence of its ionic conductivity on the sufficient degree of swelling. This becomes a problem at the temperature above 100 °C, where saturated water vapor pressure is higher than the atmospheric one. This may be overcome by elevating the pressure. Unfortunately, it is reported in the literature, that this approach results in membrane degradation. The study performed within this project has proven decline of the membrane conductivity in time under the elevated pressure conditions and at temperature above 100 °C. This trend becomes more progressive at increasing pressure and temperature. At the same time, however, no significant chemical degradation of the membrane material was detected by means of IR spectroscopy. The conductivity decline is more probably caused by excessive swelling of the membrane induced by elevated pressure and temperature. This results in destabilization of the internal oriented network of the membrane polymer inducing decrease in its conductivity. Such behavior is indicated also by the changes in the membrane sample dimensions observed during the conductivity tests. Two options of solving this problem were followed: (i) modification of the membrane structure resulting in its stabilization (ii) change in the perfluorinated sulphonated molecule structure providing resulting material with higher thermal stability.

Nafion-PTFE-boron phosphate composites

The first mentioned option represents modification of the standard perfluorinated sulphonated material based membranes. Modification is aimed to stabilise its structure. At the first stage reinforcement of the membrane by the PTFE fibres was tested. Woven mesh made of PTFE fibres was used (commercially available Nafion 417 membrane). Even more or less perfect stabilisation of the membrane sample in length and width was proven, the conductivity declined in time significantly again. This was due to its expansion in the remaining direction, membrane thickness. In order to overcome this problem, new type of reinforcement consisting of the PTFE nanofibres in the form of the porous foil was used. The membrane was prepared by the casting from the ionomer solution. Beside this type of membrane reinforcement its further stabilisation by the incorporation of the inorganic phase was tested. Boron phosphate was selected as a component suitable for this purpose. B(OEt)3 and H3PO4 were added in stoichiometric amounts to the ionomer solution prior to its casting. The mixture was homogenised and the membranes casted. Different theoretical BPO4 loadings, ranging from 0 to 20 wt.%, were used. This type of material has proven to be significantly more stable than the classical extruded homogeneous membranes. Detailed characterisation of the mechanical, chemical and structural properties of this material was performed. Changes in the functional group environment were detected, most probably caused by the presence of the inorganic phase. Even BPO4 was found to be washed out of the membrane during the conditioning period, the membrane has shown promising properties and was tested subsequently more thoroughly in the water electrolysis cell.

Alternative PFSA membranes

Second solution is to follow alternative perfluorinated sulphonated materials with modified polymer molecule structure. Aquivion™ (Solvay Solexis) has emerged as promising option. This material is being characterised by the shorter side chains. It has been proposed as an electrolyte material for fuel cells operating at temperatures above 100°C. The membrane has a higher softening point temperature than Nafion. It makes it more suitable for water electrolysis at elevated

temperatures. Different behaviour of this material was observed during the conductivity tests. After sudden decrease of the conductivity within short initiation period of the experiment, its conductivity remained stable over several hundred hours.

2. Composite membranes

Polymer membranes containing ionic liquids

Polymer supported ionic liquids (ILs) are often reported in the literature as a promising alternative proton conductive polymer electrolyte suitable for the elevated temperature and reduced relative humidity of the environment. ILs are a salts characterised by the melting temperature lower than 100 °C. A special class of them has a melting temperature lower than 20 °C. These are called room temperature ILs (RTILs). ILs are characterised by relatively high ionic conductivity, especially at elevated temperature, and by zero vapour pressure above their surface. They are studied with respect to this application, even the mechanism of the proton conduction in this environment at considered conditions (low relative humidity) is not understood yet.

Within this project attention was focused on establishment of relationship between supporting polymer and IL structure and their compatibility, selection and characterisation of the suitable ILs (preferably carrying proton and thus potentially facilitating proton transport) and finally preparation and characterisation of the homogeneous membranes based on polymer supported ILs carrying proton.

As the main representatives of the polymer supports tested poly(vinyl alcohol), PBI and its derivatives, poly(vinylidene fluoride-co-hexafluoropropylene), sulphonated PBI derivatives and perfluorinated sulphonated polymers may be given. Polymer membranes containing ionic liquid were prepared by: (a) imbibing a polymer membrane with an ionic liquid, (b) dissolving a polymer and an ionic liquid in a common solvent and casting the film or (c) polymerizing monomers in the presence of an ionic liquid. Majority of the membrane materials was prepared by method (b). These experiments revealed that the basic characteristic governing miscibility of the both phases is their similar water affinity. Further more, as it was found, in order to obtain sufficiently conductive membrane both components have to be miscible in a broad range of the concentrations. The reason consists in a need to reach sufficient concentration of IL in the polymer phase.

An interesting alternative to the combination of the electroneutral polymeric support with a traditional ionic liquid represents involvement of one or more functionalised components. It means either functionalised IL, or polymeric support. The function groups may under certain conditions facilitate proton transport across the membrane. In the first instance attention has focused on the utilization of newly synthesized ionic liquids carrying such a group. In this particular case 1-(3-sulphopropyl)pyrolidinium trifluoromethanesulphonate and 1-ethylimidazolium trifluoromethane sulphonate as promising candidates. Whereas the first ionic liquid contains the sulpho group as a possible proton acceptor, the second one allows the quaternary ammonium to be protonised and thus to facilitate the proton transport. Thus two different types of functional groups have been compared. The second approach is based on utilizing of the functionalised polymer as an ionic liquid support. Perfluorinated sulphonated polymer was selected for this purpose, mainly due to its high chemical stability.

Detail characterization has revealed only limited compatibility of the functionalized materials with the second membrane component. Nevertheless, series of the membrane samples was finally prepared and subsequently characterized. As it was found, functional groups provide significant membrane performance only under condition of sufficient humidification. It indicates, that without dissociation of the functional group in a conventional way, its contribution to the proton transport is negligible.

Even though the membranes with sufficient ionic conductivity have been prepared, their performance in the water electrolysis cell was poor. The reason seems to be limited by the transport of the proton representing the charge carrier in this technology. A second problematic aspect is the stability of the membranes in systems, where danger of water condensation exists.

3. Acid-base polymer membranes

Nafion-PBI-phosphoric acid membranes

A novel preparation procedure of homogenous Nafion-PBI acid-base blend membranes was developed and applied. Membranes were prepared covering the entire range of both polymers contents. An attempt was also made to prepare ZrP composite membranes based on the blends with high Nafion contents. Mechanical properties, swelling in phosphoric acid as well as proton conductivity of the membranes were followed in dependence of their composition and of the temperature. As it was observed, the amount of phosphoric acid absorbed by the membrane decreased with the Nafion content in the blend. It is caused by the cross linking of the polymer blend by the interaction between functional groups of both polymers. On the other hand, the membranes containing concentration of Nafion lower than 50 % were subject of at least partial dissolution in the phosphoric acid at elevated temperature. It confirms that cross linking effect induced by blending polymers of opposite polarity has improved stability of the resulting material. Lowest degree of swelling was obtained for the sample containing 88 % of Nafion polymer. It is thus possible to assume, that at this composition the cross linking has reached maximum and functional groups of both polymers are present in approximately equimolar amount. This composition of the membrane is characterized by the lowest conductivity reaching order of magnitude of 10 5 S cm 1 at 130 °C and relative humidity of environment of 16 to 18 %. With decreasing content of Nafion in the blend the conductivity increased up to a value of approximately 10 1 S cm 1 at the identical conditions. On the other hand, increasing the Nafion content from 88 % to 100 %, raised the conductivity to 0.3 - 0.9 S cm-1, depending on the level of doping with phosphoric acid.

From these experiments it followed that only membranes based on pure PBI doped with phosphoric acid, and pure Nafion doped with phosphoric acid, have reached conductivity sufficient to ensure sufficient performance of the corresponding water electrolysis unit. Unfortunately, the experimental trials in the laboratory electrolysis cell revealed insufficient durability of PBI type of membrane. Its lifetime was limited by the failure of the membrane typically after few hours of operation. Consequently the focus was directed towards PFSA membranes (Nafion and the shorter side chained Aquivion).

4. Anion exchange membranes

Heterogeneous alkaline membranes

In the field of alkaline membrane materials mainly the heterogeneous type of membranes was studied within this project. The reason consists in the higher robustness of this material type. It is due to the fact, that the matrix polymer typically protects the ion selective phase against the chemical attack from the side of the environment membrane is exposed to. This is, however, at the expenses of the membrane electrochemical characteristics. As it is known, the main obstacle in the application of the ion selective resins as a polymer electrolyte in the alkaline water electrolysis consists in the instability of the anion selective functional groups in the strongly alkaline environment, especially at the elevated temperatures, i.e. at the conditions relevant to the alkaline water electrolysis process. Therefore, in the first instance the stability of the selected functional groups representing two types of central atoms and two structural types, namely trimethylbenzylammonium, methyl pyridinium and tributylbenzylphosphonium groups were tested. Trimethylbenzylammonium has proven to be the most stable functional group amongst those tested. It was therefore used during the entire project.

The functionality of the heterogeneous membrane is closely related to its structure determined not only by the ion selective particles but also by the properties of the polymeric binder. Highly flexible linear polyethylene, low density polyethylene with a small amount of branching in the chain were evaluated as the most suitable materials. Whereas linear polyethylene provides membrane with higher conductivity, low density polyethylene is characterised by higher thermal stability. This problem was solved by the addition of the water soluble additive into the matrix polymer. Poly(ethene glycol-ran-propene glycol) was selected for this purpose. During membrane activation water soluble additive is washed out of the membrane. This is especially important in the case of the skin layer. It usually represents important barrier to the efficient charge transfer. After washing out the water soluble component, porosity of the matrix polymer increases. It improves contact between ion exchange particles incorporated into the membrane. This approach allows utilisation of the low density polyethylene (more thermally stable) as the matrix polymer without negative impact on the resulting membrane conductivity. Resulting membrane exhibits sufficient ionic conductivity and stability at least during hundred hours of electrolysis at the temperature of 70 °C without impact on its performance.

In parallel to the heterogeneous membrane development a polymer has been studied utilisable as a binder of the catalytic layer. Poly[styrene-block-(ethene-stat-butene)-block-styrene] has shown promising properties in this sense. Its properties were studied in the first instance in the form of homogeneous membrane casted from the solution of precursors. Subsequently, performance as a binder in the catalyst layer was verified.

5. Recommendations for the further membrane development

In the case of the PEM type water electrolysis materials based on the perfluorinated sulphonated materials represent so far the only polymer material possessing chemical and mechanical stability allowing for the long term water electrolysis operation. Additional important advantage represents the fact, that it does not interact in a negative way with the catalyst material and thus it doesn't influence its electrocatalytic properties. Main disadvantage represents sensitivity to the swelling. It leads to the necessity to work either at the temperature below 100 °C. At higher operational temperature two options exist. First one consist in operation at elevated pressure. In such a case stabilization of the membrane is necessary in order to keep its stability in a long term operation. Modification of the polymer molecule structure leading to the improvement of the resulting polymer thermal stability.

Second option consists in modification of this material by a component helping to keep its swelling on the sufficient level also at the low relative humidity.

In the field of the anion selective materials it is at this moment difficult to expect discovery of the new type of the ion exchange group. Searching for suitable molecule or final membrane structure offers a possibility. Nevertheless, the main issue currently represents absence of suitable alkaline polymer binder of the catalytic layer. Absence of this material leads to the necessity to use also in the most advance alkaline electrolyser KOH solution instead of the demineralised water. Copolymer materials offer an interesting option and broad spectra of possible solutions.

WP 3. Construction materials

The term "construction materials" refers to the materials used for flowplates/bipolar plates and current collectors/gas diffusion layers (GDLs).

This part of the project is focused on the use of protective coatings of tantalum metal made by chemical vapour deposition (CVD). The overall principle of this is the reduction of a gaseous precursor TaCl5 by hydrogen at 800-850oC:

2TaCl5(g)+ 5H2(g) 2 Ta + 10HCl(g)

The tantalum metal formed inside the reaction chamber deposits on the parts to be coated, when proper process conditions are applied.

A variety of materials, such as advanced steel alloys, Hastelloy, titanium, niobium and tantalum as well as certain ceramic materials, were tested for stability in acidic conditions (phosphoric acid) combined with a strongly anodic potential to simulate the conditions at the anode in an electrolyser cell. The only metallic material which had acceptable corrosion rate (<0.01 mm/yr) under the most severe conditions tested (concentrated phosphoric acid, 150 °C, anodic polarization up to 2.5 V/ Ag/AgCl was tantalum. Other promising materials were useless for various reasons. The corrosion rate of various types of stainless steel, and nickel alloys, niobium and titanium is too high at the temperatures in question (110 °C and above). Another product from Tantaline, "TantaCell", made by alloying a thin layer (1-2 micrometer) of tantalum into titanium creating a titanium-tantalum alloy on the surface rather than a pure tantalum layer was also not sufficiently stable.

The relative costs of the 2 suitable materials (c.p. Tantalum and the "Tantaline" tantalum surface treated steel) was evaluated on a theoretical basis. As the cost of producing the "Tantaline" modified solution is less than 10% of using solid Tantalum, making "Tantaline" the most suitable solution in further large scale installations.

Flow plates/bipolar plates from Tantaline treated stainless steel and Tantaline treated copper perform well in laboratory test rigs at the other partners. Standard 50µm Tantaline treatment is applied and no problems with contact resistance between catalyst, current collector and bipolar plate due to tantalum passivation have been observed. This was confirmed by measurements of contact resistance properties of tantalum and other materials after anodisation. Different shapes of flow pattern have been tantalum treated. The flow pattern has no influence on the Tantaline processing.

Stainless steel mesh and felt materials have been coated successfully with tantalum for GDL/current collectors. Two particular types of the steel felt were used for tantalum coating experiments and for further testing as GDLs. Both of them were based on 316L stainless steel felt.

The different felts were:

- 200 microns thick stainless steel felt with a wire thickness of 8 microns and a porosity of 83%.
- 500 microns thick stainless steel felt with a wire thickness of 12 microns and a porosity of 82%.

These felts were coated with different amounts of tantalum. It was found that a thin coating of tantalum was necessary to ensure that a sufficient porosity was maintained. Thicker coatings of tantalum gave mass transport limitations. But very thin coating gave a very open structure, and problems with spraying the catalyst directly onto the GDL.

As long as the tantalum coatings were thin enough to ensure the sufficient degree of openness in the GDLs no big difference was observed during the test. But the thicker (500 microns) GDL is believed to give better contact with the membrane in larger MEAs as it can provide a more efficient "spring effect".

Another important quality for the GDL is the tantalum topology on the coated felt. The difference can be seen on the SEM micrographs in figure . The topology can to some degree be controlled by the process conditions of the CVD process.

Figure 9 shows pristine steel felt, and coated felt with two different thicknesses of tantalum coating, designated "batch 1" and "batch 2". The batch 1 material has a porosity of 45% and Batch 2 a porosity of 72%.

It was found that the felt from batch 1 had far better performance than felt from batch 2 (Figure 10). It is mainly a matter of lower resistance in MEAs with felt from batch 1. Batch 1 felt has a more rough surface than batch 2, which will give more contacts point and hence a lower contact resistance. The catalytic performance is also slightly better with felt from batch 1, the reason is probably that the structure is a bit more closed and the catalyst does not penetrate as deeply into the felt structure and hence a larger amount of catalyst is available for reaction compared to an anode with the same IrO2 loading but based on felt from batch 2.

A high performance of the felt of 45% is in accordance with previous results from other groups/projects - based on titanium sinter materials - which indicate that a porosity of around 50% is optimal.

Figure 9 SEM micrographs for: A: pristine stainless steel felt, B: Tantalum coated felt from batch 1 and C: Tantalum coated felt from batch 2.

Figure 10. Polarisation curves for MEAs with different GDL batches (130oC, 1 bar).

Common properties of the two MEAs:

- Membrane: Aquivion E79-05S doped with 85 wt% H3PO4 at 150 °C and 16 hours. Thickness 60 µm.

- Anode: IrO2: ~1 mg/cm2 5 wt% Aquivion, GDL: Tantalum covered SS-felt thickness 0.48 mm.
- Cathode: Pt/C on carbon cloth, loading 0.81 mg/cm2

Corrosion products from the stainless steel base exposed during cutting and possibly compression of the felts is believed to be a problem for membrane life time. The amount of leachable ions can be reduced be treating the felt with hot concentrated hydrochloric acid prior to use. This treatment efficiently etches out exposed steel, while leaving the tantalum intact. Since tantalum constitutes about half the volume of the treated felt the mechanical integrity is not impaired significantly by leaching out some stainless steel.

WP 4. MEA fabrication

Fabrication of MEAs based on new materials

In general the MEAs for lab scale testing were prepared on the basis of the following materials and procedures:

Cathodes were prepared using Pt on carbon as catalyst, in combination with Nafion, Aquivion or PBI as the ionomer, depending on whether membrane material was going to be PFSA or PBI. The GDL was always a carbon cloth material. A catalyst ink was sprayed on to the carbon GDL. This cathode preparation was adapted without significant change from the PEM fuel cell research.

Anode catalysts was always based on IrO2 as the active component. A pure IrO2 was prepared by NTNU as mentioned previously, but other types were also used during testing of MEAs, these were IrO2 supported on TiOx or SiC/Si, as well as pure IrO2 prepared by the Adams Fusion method.

A catalyst ink (ionomer + catalyst) was usually sprayed onto the anodic GDL on a hot plate. The Decal method was also investigated, but spraying on the GDL was the most successful method, for spraying the solvent used for the ink was usually isopropanol or ethanol.

The GDL was tantalum coated steel felt as described under the section "Construction materials".

Hot pressing was generally used if the membrane involved was phosphoric acid doped. In cases of undoped Nafion or Aquivion membranes materials used for testing MEAs under pressurised liquid water conditions, hot pressing was not important, the MEAs were often just assembled directly in the cell.

The flowplates of the various labscale electrolyser cells used normally had a straight channel flowpattern.

To carry out the MEA testing various test rigs were built the partners providing the possibility of testing under steam or piqued phase conditions, as well as under acidic and alkaline conditions.

1. MEA's for acidic PEM electrolysers for steam electrolysis.

Several different membrane materials have been tested on evaluated for use in electrolysis operation at elevated temperature. Test has been conducted under steam conditions, but also at elevated pressures so the feed was liquid water.

For steam electrolysis the following types were tested in MEAs:

- Polybenzimidazole (PBI) doped with phosphoric acid (PA)
- Nafion doped with PA
- Nafion doped with an inorganic filler - zirconium phosphate (ZrP)
- Nafion doped with ZrP and PA
- Aquivion doped with PA

In a later stage of the project period the main focus has been on PFSA type membranes (Nafion® and Aquivion™) doped with PA.

The PBI membranes doped with PA showed good conductivity at operation conditions of 130 °C and atmospheric pressure, but the stability of the membrane was not sufficient for it to be a serious candidate for the electrolyte of the final MEAs of the project. Test showed that the membrane failed after very short periods. In general the membrane only lasted between 6 and 10 hours. The time of failure was depended of the thickness of the membrane and the current density and thereby the voltage it was operated at.

Nafion doped with both PA and ZrP gave a marginal better performance than Nafion only doped with PA. The performance is generally still too low to electrolysis application, although high performances were occasionally obtained (see Figure 4). A problem with Nafion membranes is that the softening point of Nafion is around 120-125 °C. This means that at the operation temperature this project is aiming for (130°C) leaves a very soft membrane with quite poor mechanical properties.

Aquivion membranes were tested because they have the same backbone as Nafion membranes which has shown good chemical stability. Aquivion has the benefit over Nafion that is has shorter side chains which provides it with a greater ability to retain the water. But more importantly, the softening point temperature of Aquivion is higher than that of Nafion. The softening point of Aquivion is around 140°C, and this means that the mechanical properties of the membrane at operation temperature are much better. Electrolysis tests have also shown that MEAs based on Aquivion membranes show quite good performance, actually at least as good results as MEAs based on PA doped PBI.

Figure 11. Polarisation curve for an Aquivion and PBI MEAs under steam electrolysis conditions, 130oC, 1 bar .

- Aquivion:
- Membrane: Aquivion E79-05S doped with 85 wt% H3PO4 at 150 °C and 16 hours. Thickness 68 µm.

- Anode: IrO2: 0.98 mg/cm2 4.8 wt% Aquivion, GDL: Tantalum covered SS-felt thickness 0.48 mm. Cathode: Pt/C on carbon cloth, loading 0.81 mg/cm2
- PBI:
- Membrane: PBI doped with 85% H3PO4. Thickness 75 µm.
- Anode: IrO2: 9.97 mg/cm2 5wt% Nafion, GDL: Tantalum covered SS-felt thickness 0.26 mm.
- Cathode: Pt/C on carbon cloth, loading 0.7 mg/cm2

2. MEA's for acidic PEM electrolysers for elevated pressure/liquid water feeding.

Within the last period of the project the activity in the field of MEA preparation and testing was focused to the electrolysis at combined elevated pressure and temperature. The elevated pressure enables to keep water in the liquid state. It exclude from possible application membranes with phosphoric acid. On the other hand, presence of liquid water ensures full humidification of membranes based on perfluorinated sulphonated polymers. Therefore main focus of MEA assembly was paid towards commercial Nafion and Aquivion membranes, and Nafion based membranes with various modifiers provided by consortium partners DTU and IMC. These pressurized MEAs generally obtained higher performances than the steam electrolysis systems so far.

The membrane materials were primarily:

Recasted Nafion, Nafion 115 and 117, Aquivion E79-05S, Recasted Nafion with porous PTFE reinforcement and/or BPO4 added (very little B or P is actually present in the completed membrane, but it appears that it there is a certain effect anyway).

The tantalum coated stainless steel felt (provided by consortium partner Tantaline) was still found as suitable gas diffusion layer. However, steel open edges dissolution can cause contamination of the membrane as well as of the catalysts. Such edges were generally present as the GDLs were cut out of larger pieces of metal felt after that the tantalum coating was carried out. Therefore a pretreatment procedure was introduced consisting of overnight heating of the GDL samples in a 20 % HCl solution.

Two thicknesses of tantalum felt were used (0.25 and 0.5 mm). The thicker one gave better results, presumably mainly due to good compatibility to the gasket thickness. A third one, 0.8 mm, was also tested, but with poor results.

The performance of electrodes was tested with commercial perfluorinated sulphonated membranes. The current density above 1 A cm-2 at 1.7 V was reproducibly reached at temperatures 120-130oC. A sample current/voltage curve measured with the electrodes prepared at DTU containing catalyst provided by NTNU and a commercial Aquivion membrane is shown on Fig. 12.

Fig. 12. The current density dependence on cell voltage. Conditions: 120°C pressure 3 bars Membrane: Aquivion, cathode 0.8 mg Pt cm 2, anode 1.72 mg IrO2 cm 2.

Another effort was focused on reducing the IrO2 loads in the anodes. The key problem represents absence of the dense microporous layer on the tantalum coated felt. Therefore, high catalyst loses occur connected with the deep penetration of the catalyst ink into the felt body. Application of the

catalyst ink onto hot GDL solves this problem only partially. Another issue represents very small catalyst loading raising the danger of its non-homogeneous distribution over the electrode missing microporous layer. Therefore also catalysts deposited on the different supports were used. Presence of catalyst support increases its volume, and it thus makes its uniform distribution more easily achievable. In addition, larger catalyst particles hardly penetrate into GDL structure. However, good results were obtained when applying the unsupported IrO2 from NTNU. Finally, loadings of 0.8-1.5 mg IrO2 cm 2 were found to be sufficient for the anode.

The loadings of 0.5- 0.8 mg Pt cm 2 for cathode were found to be sufficient.

For more detailed testing, MEAs based on the membranes prepared by the project was selected, namely casted Nafion membrane supported by porous PTFE with or without 5 wt.% BPO4 added. The current/voltage dependence of MEA based on mentioned materials is shown on Fig. 13. In this case a current density above 1.0 A cm-2 at cell voltage of 1.66 V was reached, and furthermore 2.0 Acm-2 at 1.85 V at 120oC.

Fig. 13. The current density dependence on cell voltage. Conditions: pressure 3 bars Membrane: recasted Nafion with 5 wt.% BPO4 additive supported by porous PTFE, cathode 0.5 mg Pt cm 2, anode 0.79 mg IrO2 cm 2 (catalyst IrO2/TiOx), electrolysis temperature is indicated in the figure inset.

3. Comments to the overall technical concept of acidic electrolysers

On the basis of the work on acidic MEA development carried out by DTU, ICTP and NTNU it was decided to chose for the upscaled MEAs for testing at IHT, that the operating conditions should be feeding of liquid water, and moderate overpressure (in the range of 3 bars), and temperature 120oC.

This set of conditions provided a higher performance than steam feeding at ambient pressure.

For the pressurized liquid water situation the doping of the PFSA membrane by phosphoric acid was unnecessary, as the pressure ensures that sufficient water is retained in the membranes to allow them to maintain and actually improve their protonic conductivity. From one point of view this would in turn reduce the corrosion of the inside of the cell, due to the absences of phosphoric acid. However, on the other side the flow of a liquid phase through the cell will provide an easy route of removal of corrosion products. That would be expected to increase corrosion.

As described in WP1 section, "Catalysts", phosphoric acid, or rather H2PO4- , tends to adsorb strongly on IrO2, and thereby decrease its catalytic activity. This is of course a likely reason for the better performance obtained by the pressurized system compared to the steam fed system using phosphoric acid doped membranes.

However, the inhibiting effect observed in the actual MEAs does not seem to be quite as important as expected on the basis of the experiments descriped in the "Catalysts" section. Reasons for this may be that the effect becomes less important, when the temperature is increased, or that free H3PO4 is protonised to H4PO4+, due to the "superacidic" properties of the sulfonic acid groups in the PFSA membranes. That would decrease the activity of H2PO4- , and thereby reduce its inhibiting effect.

As already said, PBI membranes doped with H3PO4 were apparently not stable under electrolysis conditions. The reason for this is not yet understood, and the question will probably be a matter of

further investigation within other projects. However, they were not an option for further testing within the frame work and time scale of WELTEMP. The focus had to be on PFSA membranes with or without modifications, as described above.

4. Alkaline MEAs for liquid water feeding at elevated temperatures.

MEAs for upscaled testing were prepared as follows:

The alkaline membrane used in the MEA is a material obtained commercially and used as is without further treatment.

The cathode catalyst used for the production of electrodes was the Ni/C based material mentioned in the WP1 section.

The anode catalyst used for the production of electrodes was a mixed oxide material also mentioned that section

Cathode electrode preparation procedure:

A 13 cm diameter disc of nickel foam was pressed to a uniform thickness of 0.5 mm. A catalyst paste consisting of the Ni/C HER catalyst and PTFE was prepared by mixing vigorously the powdered catalyst and a suitable quantity of a 60 wt% aqueous PTFE suspension (to give a final PTFE content of 10 wt% relative to the catalyst material) together with a small amount of demineralised water. The paste thus obtained was applied to one face of the nickel foam disc. The coated electrode was then pressed to obtain a uniform thickness of 0.7 mm. The final catalyst loading was approximately 30 mg/cm2.

After drying over night the coated electrode was heated under a flow of argon and then allowed to cool to room temperature under continued argon flow. The purpose of this heat treatment was on one hand to remove the surfactant material contained in the PTFE suspension and on the other to sinter the PTFE to form a more uniform and hydrophobic catalyst layer.

Anode electrode preparation procedure:

A 13 cm diameter disc of nickel foam was pressed to a uniform thickness of 0.5 mm. A catalyst paste consisting of the developed mixed oxide OER catalyst and PTFE was prepared by mixing vigorously the powdered catalyst and a suitable quantity of a 60 wt% aqueous PTFE suspension (to give a final PTFE content of 5 wt% relative to the catalyst material) together with a small amount of de ionized water. The paste thus obtained was applied to one face of the nickel foam disc. The coated electrode was then pressed to obtain a uniform thickness of 0.7 mm. The final catalyst loading was approximately 60 mg/cm2.

After drying over night the coated electrode was heat treated and then allowed to cool to room temperature.

These components as well as membranes were then assembled directly in upscaled cells for testing.

Preliminary low temperature test cell results:

During the project period various alkaline MEAs were prepared described above for use in a small test cell (cell active area 9.6 cm2). The MEA and test cell characteristics are as follows:

- Anode and cathode electrode thickness 0.7 mm (in cell compresses to around 0.5 mm)
- Membrane thickness: Dry 70 micron; Wet 80 micron - (negligible)
- Liquid and gas diffusion layers (need to fill about 3.5-4 mm on both sides)
- Flow fields consisted of compressed nickel foam (3.9 mm)

The test cell is made of stainless steel current collectors with electrolyte flow at the anode side and no liquid flow at the cathode side. The outlet hydrogen pressure can be adjusted up to 30 bar. In all the experiments described here the hydrogen outlet pressure was set at 20 bar. These cells operate at around 40 °C and were not designed for high temperature operation.

Characteristic polarisation curves for the alkaline MEA are shown in Fig. 14. The cell is in principle fed with a liquid electrolyte in order to maintain sufficient ionic conductivity of the membrane, i.e. the membrane has to be kept soaked with ions. For this concept the typical salt to be added would be KOH. Thus, a pool of such electrolyte is kept circulating, and extra water is continuously added corresponding to the amount consumed. This is similar to the situation in a traditional alkaline electrolyser.

The red curve in Figure 14 was obtained with an electrolyte consisting of 1 wt% aqueous K2CO3 and the black curve with 5 wt% aqueous KOH. The MEA performs at a cell voltage approximately 200 mV less with a KOH electrolyte as opposed to the K2CO3 electrolyte. The difference can be seen throughout the entire potentail scan apart from the initial low current density kinetic part. This suggests that the difference is essentially related to the difference in ionic conductivity of the membrane in the OH- or CO32- forms. However, after longer periods of testing a steady performance is reached, and the difference between the two cells was decreased to about 50 mV. Consequently, the difference in ionic conductivity of the membrane in either form CO32-, OH- has little effect in the overall cell performance.

Figure 14 Polarisation obtained with the ACTA alkaline MEA (5 mV/s). Tcell = 40 °C.

Figure 15 shows an extended life test for the MEA with the K2CO3 electrolyte (> 600 h) which shows continued stable performance. Life tests have continued with this MEA and over 6000 hours of operation has now been achieved in test cells.

The reason for switching to the non KOH electrolyte is related to stability concerns with respect to the alkaline exchange membrane. The functional groups most commonly used in polymeric anion exchange materials are quaternary ammonium groups (NR4+). One of the most predominant decomposition mechanisms for these materials is the Hoffman elimination whereby the OH- anion (a very aggressive nucleophile) displaces the ammonium groups in the polymer backbone. This leads to a loss of ion exchange capacity and consequently ionic conductivity. This process is also known to be accelerated at higher temperatures. Utilizing a carbonate electrolyte retains sufficient ionic

conductivity at the same time removing the high concentration of OH- that can cause rapid decomposition. This will be of vital importance when these materials are used at the temperatures to be investigated in the project (120-200 °C).

Figure 15 Life test (> 600 h) obtained with the ACTA alkaline MEA (475 mA/cm2). Tcell = 40 °C.

5. Comments to technical concept of alkaline electrolysers

Anode and cathode electrodes containing the non PGM catalysts developed by ACTA for the alkaline electrolyser were prepared and optimised. Both electrode types were prepared by applying PTFE containing pastes onto a nickel foam support material, followed by a high temperature sintering process. The performance of these electrodes mounted together with a commercial anion exchange membrane at low temperature (40 °C) was investigated in the test cell. Performance with a 1 wt% K2CO3 flowing electrolyte at this temperature was stable over a long period (> 6000 h). At a working current density of 475 mA/cm2 the stable cell voltage was around 2.2 V. Although this performance is far from project objectives (Vcell of 1.5 V at 1 A/cm2), the performance of this MEA at the desired temperature of 120 °C was still unknown. Furthermore it must be emphasized that PTFE is not the optimal binder for the catalyst layers, future research and development focusing on such materials will probably improve things considerably.

In order to study the performance of the alkaline MEA under HT conditions sets of larger electrodes were prepared for testing in the prototype stack at IHT (11 cm diameter of active electrode area). These were shipped together with sheets of anion exchange membrane, which could be cut to the correct shape and mounted in the prototype stack.

WP 5. Prototype stack

A prototype electrolyser stack and test rig was built for demonstration and evaluation of polymeric electrolyte membrane assemblies at temperatures in the range of 120-130 oC.

On the basis of the results discussed above, it was decided to design the test rig as well as the stack for being fed by pressurized liquid water, rather than by steam. In addition this allowed using the same setup for both acidic and alkaline MEAs.

However different designs of flowplates were used for acidic and alkaline cells, respectively. Also, the alkaline cells need a circulating solution of KOH or K2CO3, whereas the acidic cells need only circulating pure water.

The design af the upscaled cells and stack at IHT is based on a modular system. This provides the possibility to test single cells, several stacked cells or many stacked cells using the same setup. Each cell can always be monitored individually. Inside each cell, MEAs as well as porous current collectors of varying thickness can be placed and tested due to the possibility to insertion of spacers.

The alkaline cells are initially set up to be used for working pressures of 3-7 bars, i.e., but the hardware part is able to withstand up to 70 bars. The cells are circular, and the active part of the electrodes has a diameter of approx. 110 mm, i.e. an area of 95 cm2. The design provides the

possibility to test one single cell, several stacked cells - which may be different from each other - using the same setup. The flow fields consist in this case of compressed nickel foam.

The alkaline PEM systems is considered quite important, as it was demonstrated that reasonable durability is within reach, and that at the same time non-noble element catalysts can provide good performances compared to noble element catalysts under similar conditions. On the other hand further development of polymers, particularly binders in the catalyst layer still needs considerable effort.

The basic components and test conditions for the up scaled prototype stacks can be summarized as follows:

Operating mode:

The working mode should be liquid phase water under pressure rather than steam electrolysis. This is based on the fact that for the acid case the highest performance was clearly obtained for pressurised mode, and for the alkaline case steam electrolysis is not yet an option

Acidic case:

Cathode

Essentially standard fuel cell electrodes with platinum on a carbon support are used. This means a Pt loading of 0.7-0.8 mg/cm2 with a 40 wt% Pt/C mixture on a wet-proofed carbon cloth. The carbon cloth works as the GDL in the electrode. The binder in the cathode should be a PFSA ionomer which has good compatibility with the recommended membrane. The amount of binder in the electrode should be between 25 and 30 wt% compared to the amount of Pt.

The total thickness of the cathode is approx. 250 microns.

Further optimisations in both loading and binder content should be done in the future.

Anode

IrO2 is used for the oxygen evolution catalyst. A special preparation method for this compound was developed during the project, providing a more chemically resistant material. The loading should be around 1 mg/cm2 IrO2 Aquivion ionomer is used as the binder in the catalyst layer, corresponding with the recommended membrane. The catalyst is sprayed directly to the GDL. The anode GDL is a tantalum coated stainless steel felt with a thickness of around 500 microns and a porosity of approx.50 %.

Further optimisation for the IrO2 loading and the binder content should also be done in the future.

Membrane

Aquivion type membranes (short side chained PFSA) are used. It has a thickness of approx. 50 microns in dry conditions and approx. 60 microns under fully hydrated conditions. A thicker Aquivion membrane could be used, but from the MEA testing done at DTU no need of a thicker membrane has been observed. A thicker membrane would just result in a larger resistance in the system

Very recently it was demonstrated within the project that PFSA reinforced Nafion membranes having superior properties can be prepared. It therefore seems likely that for future work such reinforced Nafion or Aquivion membrane will be a better candidate, but more development will have to be done in order to ensure sufficient uniformity and reproducibility.

Operating conditions for acidic cells/stack

- Temperature: 120-130 °C
- Pressure: 3 bar total pressure, and above
- Flow pattern: Straight, parallel channels are used.

Alkaline case:

Cathode

New, non-noble metal catalyst is used, GDL is made of nickel foam.

Anode

New, non-noble metal catalyst is used, GDL is made of nickel foam.

Membrane

Although new membranes have been prepared within the project, a commercially available anion exchange membrane type is initially used due to its well established uniform quality.

Operating conditions for alkaline cells/stack

- Temperature: Testing in the whole range from 40- 120°C
- Pressure: 3 bar total pressure, and above
- Flow pattern: Nickel foam.

Potential Impact:

During the WELTEMP project significant and important results were obtained, which will have impact on the general development of water electrolysers for hydrogen production:

New proton conducting polymer membrane materials with reinforcement of a porous PTFE material with very significantly improved performance as well as strongly improved mechanical properties were prepared. Such materials do not seem to have been available to European industries within the field. A reinforcement is most likely crucial to the development of PEM electrolyser cells for very high pressure, like 70 or 100 bars. It seems plausible that there is going to be a demand for such high pressure electrolysers, because they can potentially deliver compressed hydrogen considerably more energy efficiently than an electrolyser working at ambient pressure followed by a mechanical compression step. There is a need for more research on these membrane materials before they can be commercialized, but it is clearly expected that partners in WELTEMP will intend to go within the matter the future, financed by various sources. It is emphasized that the same idea is developed at various places outside Europe (various places in China, and Giner Technologies in USA uses a perforated PTFE film as reinforcement for their high pressure electrolysers).

Steam electrolysis was - for the first time? - carried out in a PEM electrolyser cell. In general the performances obtained were not as good as for pressurized cells fed with liquid water, but in a few cases very high performances were indeed obtained. However, this phenomenon is not yet understood. In any case, the possibility to carry out steam electrolysis opens some new options for future research and development. One of the advantages of this concept could be that there is no flowing liquid phase to continuously remove corrosion products from metallic parts, membranes or catalyst materials, and thereby slowing down any corrosion taking place.

One can of course imagine increasing both pressure and temperature further, while still keeping the water as steam. This will require materials - not least membrane materials - capable of working at considerably higher temperatures than 130oC. This will most likely involve electrolyte materials based on inorganic proton conductors, eventually with organic binders to achieve sufficient mechanical stability. The experience obtained during WELTEMP has been the basis for starting a nationally founded project in Denmark within this field (Danish Council for Strategic Research). This is project of more fundamental character than Weltemp, but all three Danish partners in Weltemp are also involved in this project as partners.

A requisite for steam electrolysis in PEM cells is that it was discovered that PFSA membranes (Nafion, Aquivion) can be doped with phosphoric acid, and thereby made conductive at temperatures higher than 100oC, when they are used in electrolysis mode - in contrast to when they are used fuel cell mode, where for some reason no current at all can be pass through them! (a paper dealing with this "diode effect" is being worked out).

Significant progress were made within the project with respect to demonstrating the concept of the alkaline PEM electrolyser: Alkaline membrane materials were demonstrated in labscale electrolysers. In addition, new electrocatalysts for both hydrogen evolution and oxygen evolution were developed, which do not contain any noble elements. Usually it has been claimed that alkaline membranes are not sufficiently chemically stable, but here a long term experiment was carried out. However it still remains to be seen how far the temperature can be rised. Furthermore there is a demand for the development of suitable binders for the catalyst layers for such electrolysers, to replace the less

efficient PTFE used in the Weltemp activities. This is presumably the most important step to be taken to lift the performance to the desired level.

The potential to avoid any use of noble elements makes this technology potentially far cheaper than the PEM technology based proton on conducting membranes, where Pt and IrO2 are needed. Thus, it is recommended to foundations and policy makers that this type of electrolysers should receive much attention/support in the very near future and further on.

Concerning construction materials for PEM electrolysers, a quite new option has been introduced by Weltemp: Tantalum coated steel felt and bipolar plates as an alternative to titanium metal sinter materials and plates of titanium. The use of refractory metals like titanium of tantalum in PEM electrolysers is required to resist the anodic potential combined with acidic conditions at the anode. Until now titanium has been the completely dominating material to be used, but the corrosion problems are strongly increased, when the temperature is elevated, and even more, if in addition the pressure is increased (that means higher oxygen pressure). In the case of the use phosphoric acid doped membrane materials it was demonstrated that titanium is completely useless, as it has an unacceptably high corrosion rate.

Furthermore it was also demonstrated by Weltemp that tantalum possesses much better electrical contact resistance properties than titanium, which means lower Ohmic resistance in the cell/stack.

The tantalum coating by chemical vapor deposition (CVD) has rather recently become a commercial process, and the task to coat porous steel felt, was a new activity to Tantaline A/S initiated as a part of Weltemp. There are of course issues concerning how to optimize the process with respect to treating the porous felt in such a way the price finds a suitable level. Such work is however in progress.

It must be mentioned, that the tantalum coated felt has already been introduced in other water electrolyser projects and developments, including the EU projects Primolyzer I and II.

The objective to have stack of PEM cells running for long time test was not achieved within the project period, however such work will continue after the deadline of the Weltemp project. A strong network was created as a result of the collaboration, and it is clearly expected that the water electrolysis activities will continue in the future one way or the other.

Weltemp has adressed materials and technologies within three different concepts of PEM electrolysers: 1) Steam electrolysis at ambient or low pressure on the basis of proton conducting (acidic) membrane electrolytes, 2) Electrolysis of pressurized water on the basis of proton conducting (acidic) membrane electrolytes. 3) Electrolysis on pressurized water using alkaline polymeric electrolytes. However, it is rather clear that in the nearer future the high pressure technologies are the most easily adapted to use for storage of energy from renewable sources.

It is believed that a wider use of water electrolysis for hydrogen production which does not rely on fossil fuels is of the outermost importance to the future. This concerns hydrogen for use as an energy carrier but also for production of ammonia for fertilizer use. The commercial experience made in the last years by IHT has shown that the market related to the renewable energy sources and especially for the storage of this energy in the form of hydrogen produced by electrolysis is already increasing very fast.

However, it seems that the spreading of combined renewable energy sources and hydrogen generators to store excess energy in periods where the production is larger than the consumption, does not at all

take place at a sufficient rate - the carbon dioxide content in the atmosphere is still increasing at rate which is unacceptably high when taking into account to today´s knowledge about the Earths atmosphere and its physics and chemistry.

In all possible applications, a main parameter in the hydrogen production process is clearly the energy efficiency. In the case of the electrolysis, the costs of the electricity represent around 80% of the hydrogen production costs. Therefore, to become more and more competitive compared to other production processes, and thereby ease its wider use, it is mandatory to design and realise an electrolysis system which has the highest possible performance and efficiency. The Weltemp project is an attempt to introduce various new technologies, particularly new materials, that provides the possibilities to increase the efficiency to levels higher than todays commercial technology. As already said several new ideas showed promising results. However it became clear during the project period, that the new technologies still needs more research and development before a wider use can take place. There are of course of other groups doing the same kind of activities, but until now no definite breakthrough has occurred that improves the efficiency significantly compared to the present alkaline technology, and at the same time is economically feasible. Thus, the competition is still going on, and it must be assumed that the region in which such a breakthrough takes place will benefit very considerably from it in the future. To our opinion further effort by European enterprises and universities is highly desireable.

Dissimination activities has been carried by publication in international journals (peer- reviewed) and by participation in conferences by the project participants. Thus, the project has been represented at international conferences (in USA, Denmark, Czech Republic, Ukraine, France, China and Greece.), and more than 17 different contributions were presented this way.

In addition to this, water electrolysis has become a subject of higher priority than previously in the education of students at bachelor and master level, particularly at DTU and ICTP/IMC, i.e. a considerable number of bachelor and master students were educated within the field of water electrolysis as consequence of the project. It is hoped, that these will spread some of their knowledge around to their future organisations and colleagues.

The following courses at ICTP now involve materials at produced within the WELTEMP project:

- "Electrochemical Technology"
- "Electrochemical Engineering"
- "Applied Chemical Processes"

Similarly, at DTU the course "Hydrogen and Fuel Cells" now contains an exercise and theory of water electrolysis.

Furthermore PhD students were of course a significant part of the man power within the project, some financed mainly by WELTEMP, and others to a higher or lower degree financed by other projects (3 at DTU, 2 at ICTP, 1 at NTNU and 1 at IMC). Some of these will stay at their universities and will influence future research projects as well as take part in teaching.

An information booklet was worked out and it is a part of the informative poster used at various occasions (International Forum of Science and Technique, Scientia Pragensis, Research Connections http://ec.europa.eu/research/conferences/2009/rtd-2009/index_en.cfm)

Furthermore, staff of WELTEMP have been represented at "Open House" events, both at DTU and at ICTP:

- DTU Chemistry staff have represented WELTEMP activities at an annual open one-day house for students in November at DTU, i.e. in the years 2008, 2009, 2010.
- IMC organised "Institute Open Days" for students and public, where results and international cooperation were presented.

In a similar way ICTP staff were present at the following events:

- Day of the Open Doors, ICT Prague, November 2008, 2009, 2010.
- Chemistry and Fuels, Prague, 18.5. 2011
- In Coffee Bar with Scientist, Kladno, 18.5. 2011
- Science on the Streets, Prague, 21.9. 2011

Furthermore, ICTP has presented WELTEMP philosophy and results within the "My Science" project (http://www.my-science.eu/) and hosted a journalist in the laboratory.

The WELTEMP project established contact to another parallel water electrolysis project, "Primolyzer" also financed by the Commission, but through the FCH-JTI. Primolyzer (Pressurised PEM Electrolyzer stack) is coordinated by IRD Fuel Cells A/S, also in Denmark. Primolyzer is working on increasing the working pressure rather than the temperature. However, elevating the pressure, like increasing the temperature as in WELTEMP, induces increased corrosion problems in a somewhat similar way.

A common workshop was organised by the coordinators of the two projects, and took place at Department of Chemistry at DTU in Denmark in January 2010.

Various ideas were exchanged, and in particular some tantalum coated steel felt prepared by Tantaline A/S was delivered to Primolyzer for testing. Elevated pressure causes increased corrosion problems just like elevated temperatures, and that makes alternatives to titanium important.

The concept of porous tantalum coated stainless steel current collectors was later included in the application for the second part of Primolyzer, submitted in August 2011.

During Autumn 2011 WELTEMP, Primolyzer and a third project NEXPEL ("Next generation PEM electrolyser for sustainable hydrogen production", coordinated by SINTEF in Norway), have initiated the organisation of a workshop dealing with water electrolysis in general. Thus, the plan is to invite speakers representing not only PEM technology, but also SOEC and alkaline technologies. The meeting will take place either in Copenhagen or in Brussels, and will be a mixture of technical contributions describing the status of techniques, and more political/economically oriented contributions. The idea is to generate an overview of the status of water electrolysis from both a technologic and a political and economic point of view. It is the hope to attract some attention from

policy makers. EU will be chaired by Denmark in 2012, and that could be a reason for placing the workshop in Copenhagen as an alternative to Brussels.

It must also be mentioned that in Denmark, a "Water Electrolysis Strategy Group" has been settled under the Ministry of Energy and Transport, and that the Energy and Materials Science Group, DTU is represented here by Assoc. Prof. Jens Oluf Jensen.

"Czech Membrane Platform" monitors the activity of the members (here IMC), and makes this information public.

Other dissimination activities carried out by ICTP were as follows:

- Project information was published in the Parliament Magazine (http://www.e-pages.dk/dods/81/ page 28)
- Participation in the conference 'Price for inovation' organised by the 'Association for Innovative Entrpreneurship' and co-organised by the Parlament of the Czech Republic.
- Periodic reports were delivered to the Ministry of Education, Youth and Sports responsible in the Czech Republic for the research and technological development.

List of Websites:

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