

PEM water electrolyzers: evidence for membrane failure in 100 kW demonstration plants

S. STUCKI, G. G. SCHERER

Paul Scherrer Institut, CH 5232 Villigen PSI, Switzerland

S. SCHLAGOWSKI

Solar-Wasserstoff-Bayern GmbH, D-92431 Neunburg vorm Wald, Germany

E. FISCHER

Aare-Tessin AG für Elektrizität (ATEL), CH 4601 Olten, Switzerland

Received 26 September 1997; accepted in revised form 18 November 1997

The long term behaviour of two 100 kW proton exchange membrane (PEM) water electrolyser plants is analysed. The systems had to be shut down due to problems with excessive levels of hydrogen in the oxygen product stream. The time to breakdown was different by a factor of nearly 10 from plant to plant. Post mortem analysis of the cell stacks revealed that the Nafion[®] 117 membrane is the weakest part in a PEM electrolyser regarding long term performance. Substantial thinning of the membranes in the stacks was detected. The degradation process was found to depend on the position within an individual cell, as well as of the position of the cell in the electrolyser stack. The dissolution process proceeds from the interface between the cathode and the membrane, is not specific with respect to the ion exchange groups, and is most likely triggered and/or enhanced by local stress on the membrane.

1. Introduction

The Membrel electrolyser technology was developed by ABB (formerly Brown, Boveri Ltd), Switzerland, over the years from 1976 to 1989 [1]. The technology is based on the use of a polymeric proton exchange membrane as the solid electrolyte ('polymer electrolyte membrane') and was first proposed by General Electric for fuel cell, and later, electrolyser applications [2, 12].

Ultrapure water is fed to the anode structure of a Membrel electrolysis cell which is made of porous titanium and activated by a mixed noble metal oxide catalyst. The membrane conducts hydrated protons from the anode to the cathode side. Appropriate swelling procedures have led to low ohmic resistances enabling high current density operation of the cells [3]. The standard membrane material (Nafion[®] 117) has been supplied by DuPont. The cathode of a Membrel electrolyser consists of a porous graphite current collector with either Pt or, in more recent designs, a mixed oxide as electrocatalyst. Individual cells are stacked into bipolar modules with graphite based separator plates providing the manifolds for water feed and gas evacuation. The operation of the cells leads to electroosmotic water transport through the membrane from the anode to the cathode side.

The technology has been demonstrated on a 100 kW commercial scale in two units: unit Stellram/ATEL (1987–1990 and 1990–present) and unit SWB,

Solar-Wasserstoff-Bayern GmbH (1990–96). The operation of these two plants has successfully demonstrated the feasibility of the technology for industrial hydrogen production. It has revealed as well that the life time of the electrolysis cells is limited. In order to identify the weak points of the technology the present paper analyses the operating data with respect to cell failure and presents the findings of the post mortem analysis of the electrolyser cells.

2. The role of Nafion[®] as electrolyte; properties

Perfluorinated sulfonic acid membranes such as Nafion (Du Pont) have been shown to be extremely resistant to the oxidative power of oxygen and even ozone [4] evolving anodes. Nafion is a copolymer of tetrafluorethylene and a perfluorinated vinyl-ethersulfonylfluoride [5]. This latter monomer gives rise to side chains with pendant sulfonic acid sites. The polymer morphology and the related properties of these membranes have been investigated comprehensively with respect to various applications [6]. An ion cluster model was deduced from structural and transport data, concluding that phase separation occurs in these polymers [7]. The water uptake of membranes and the resulting size of the ionic clusters is determined by the pre-conditioning temperature of the swelling process in water. Ionic transport (e.g., proton transport) is described in this model as a hopping process from one cluster to the next one,

assuming that clusters are connected by channels [8]. Proton mobility and hence the specific resistance is determined by the 'hydration shell' (number of water molecules per sulfonic acid group $N \text{ H}_2\text{O}/\text{--SO}_3\text{H}$) [9].

Recently, this cluster model has been questioned on the basis of X-ray data of differently swollen membranes, postulating a lamellar structure for the Nafion[®] polymer [10].

The amount of electroosmotic water flow from anode to cathode depends on the equivalent weight, the pretreatment (swelling) temperature of the membrane, and the operating temperature of the electrolysis cell. The number, n , of water molecules per proton transported across the membrane has been observed to be in the range $n = 2\text{--}5$.

Gas permeation across the membrane depends on the thickness of the membrane. For membranes of different equivalent weight oxygen permeation can be separated into a solubility and diffusive component in the aqueous and the hydrophobic perfluoro-phase of the membrane [11]. Gases permeating the membrane clearly affect the performance of an electrolyser. They lead to losses in current efficiency and, worse, if they do not recombine at the counter electrode(s) they contaminate the product gases. Levels of 4% hydrogen in oxygen, and likewise of 4% oxygen in hydrogen, are explosive and must be avoided for safety reasons. Another detrimental effect of gas diffusion in electrolyzers can affect membrane stability: if hydrogen and oxygen recombine inside the membrane to form hydrogen peroxide the latter has been found to lead to degradation of the early membrane materials [12].

Degradation of Nafion[®] membranes has been observed in PEM cells, fluoride ions have been observed in the cathodic reactant water of fuel cells and there have been claims that traces of ions are a necessary condition for the electrode-electrolyte contact of a PEM cell [13].

3. Description of demonstration plants

3.1. Stellram/ATEL plant

The first commercial-scale Membrel electrolyser was installed in 1987 at Stellram SA, a metallurgical speciality company, in Nyon, Switzerland. The unit was designed to produce up to $20 \text{ Nm}^3 \text{ h}^{-1}$ of hydrogen at a pressure of 1–2 bar. The hydrogen was used for providing reducing atmospheres in high temperature annealing processes. The plant consisted of 120 cells of $20 \times 20 \text{ cm}^2$ of active area each, grouped into four modules of 30 cells, and electrically connected in series. The modules were arranged into two vertical stacks which were compressed individually by a hydraulic system with a force of 350 N cm^{-2} . The individual cells were composed of a sheet of Nafion[®] 117 which was coated by a thin layer of Pt on one side. The Pt layer was applied using a proprietary electroforming technique and was used as the cathode catalyst. Prior to applying the catalyst,

the membranes were hydrated in an autoclave at $T = 130^\circ\text{C}$ for 2 h in ultrapure water. After cooling down, the membranes were treated in 1 M HCl for 30 min and subsequently rinsed in demineralized water. This procedure was applied to all membranes investigated in this study.

The anode catalyst for oxygen evolution was a Ru/Ir mixed oxide, applied as a PTFE-bonded powder to the surface of a porous Ti current collector. The porous current collector for the cathode consisted of a graphite-PTFE-composite bonded to a brass wire mesh. Water is circulated through the anode manifolds in order to maintain equal temperature distribution over the entire membrane/electrode area. The temperature of the system is measured at the outlet of the anode loop. The purity of the gases was measured continuously using online instrumentation. A simplified layout of the plant is shown in Fig. 1.

The nominal operating conditions for the plant at start-up were: 400 A (i.e., 10 kA m^{-2}), at 80°C . Cell voltages at these operating conditions were typically of order 1.75 V. The plant was operated under varying load, according to the hydrogen needs of the metallurgical processes, for a total of $\sim 15\,000$ hours before it had to be shut down completely in 1990 because the hydrogen concentration in the oxygen had exceeded the safety level (3%). By this time the voltage across a number of cells had dropped drastically indicating short circuits within these cells as

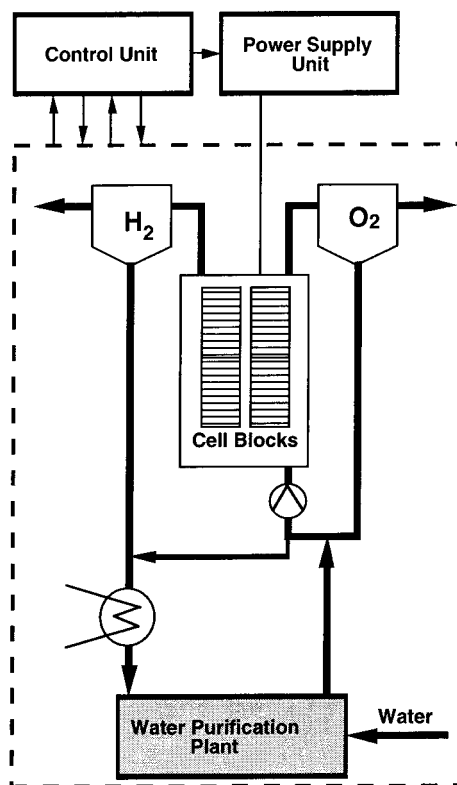


Fig. 1. Simplified layout of 100 kW Membrel electrolysis plant. Water is circulated in the anode loop using a circulation pump. Water collected in the cathode gas separator (i.e., electroosmotically pumped water) is fed to water purification plant, together with water blown down from anode loop. Bipolar cell stacks are electrically connected in series. Water flow in cells is parallel.

the cause for gas leakages and gas purity problems. Stellram SA subsequently discontinued their on-site production of hydrogen. The 120 cells were disassembled at the Paul Scherrer Institute. After replacing all the membranes and electrocatalytic layers and part of the current collectors and bipolar plates, the plant was reassembled and transferred to an experimental site of the Swiss electric utility company ATEL at Niedergösgen/Switzerland in 1991. The plant has been in intermittent operation ever since and has accumulated over 5500 operating hours today. Except for the cathode catalyst, the cells in the revamped ATEL version were made up using the same materials. The ATEL plant was equipped with cathode electrocatalysts prepared from mixed oxides of Ir and Ru [14] and applied to the cathode current collector surface.

3.2. *The Solar Wasserstoff Bayern (SWB) plant*

The design of this second Membrel demonstration unit was slightly different from the Stellram plant. The major differences were: the thickness of the bipolar plates of the cell stacks was reduced. All 120 cells were assembled into one stack consisting of three modules of 40 cells each. The hydraulic compression of the cell stack was replaced by a mechanical system with springs to allow for thermal expansion. The nominal clamping pressure was the same as in the Stellram/ATEL plant. As in the revamped ATEL plant, the cathode catalyst consisted of the same material as the anode catalyst (Ir/Ru oxide).

4. Experimental

4.1. *Disassembly of cell stacks from 100 kW units*

The individual cells were disassembled and visually inspected. Membranes were separated from the porous current collector plates and sealed into polythene bags for storage. Deionized water was added to maintain the hydration of the material. In order to remove adhering powder agglomerates (electrocatalyst and loose current collector material) the membranes were, prior to measurements, subjected to ultra-sonic treatment in deionized water for 15 min, followed by careful cleaning using a jet of water.

4.2. *Measurement of membrane thickness distributions*

The thickness distribution over the whole active area of the membranes was measured manually in the case of the membranes from the Stellram plant using a Micro-Hite gauge, which measures, with a calibrated tip, the elevation of an object relative to a reference plane. The thickness was measured at nine regularly distributed points on the $20 \times 20 \text{ cm}^2$ active area of the membrane. For the measurements of the samples from the SWB cells, an automatic instrument (Wenzel Präzision), which scans the membrane at preselected points, was available. The accuracy of

both instruments is in the order of $\pm 2 \mu\text{m}$. The thickness of the SWB membranes was measured at 6×6 points of the membrane area, including, as a reference, those parts which were clamped between the cell gaskets and, hence, were not exposed to electrode reactions at their surface.

4.3. *Equivalent weight measurements*

For determining the equivalent weight of membranes, samples were boiled in HNO_3 (33%) for 2 h and washed free of acid afterwards with deionised (18 M Ω) boiling water in several consecutive operations. After this treatment each membrane was immersed in a defined volume of 0.5 M KCl solution at room temperature and kept there for 2 h. The liberated acid was titrated with 0.1 M KOH to pH 7. The obtained potassium form of the membrane was washed free of salt and dried in a vacuum oven (60 °C, 20 mbar). The equivalent weight was calculated from the base consumption and the weight of the dried membrane, corrected for the difference between K^+ and H^+ .

Membranes tested in an electrolysis cell were treated in 3 M HCl at 80 °C to regenerate the proton form and subsequently washed acid-free, before determining their equivalent weight as described above.

4.4. *Laboratory experiments with single 30 cm² multiple membrane cells*

Nafion[®] 117 membranes were tested in the laboratory at 80 °C in stainless steel single cells of 30 cm² active area using standard Ir/Ru anodes and Pt black cathodes.

5. Results

5.1. *Inspection and thickness analysis of membranes from Stellram plant*

The reason for the shut-down of the Stellram plant was hydrogen levels in oxygen exceeding the safe level of 3%. At the same time the operators realised that the cell voltages of some of the 120 cells had dropped significantly below average. When disassembled, eight out of the total number of 22 cells with reduced voltage showed areas on the membrane of several cm² which were damaged to the point that anode and cathode were short-circuited.

In addition to the 22 membranes which had been marked by the operators as being low in voltage, an equal number of membranes was chosen randomly from the remaining 98 cells. The thickness distributions over the active area of these membranes were, after careful cleaning, measured. The average thickness of the membranes was calculated from nine measurements at different sites on the active area. The results are summarised in Fig. 2 which shows a plot of the average thickness for membranes which had been marked by the operators (cell voltages below average) and from the random sample. The standard deviation

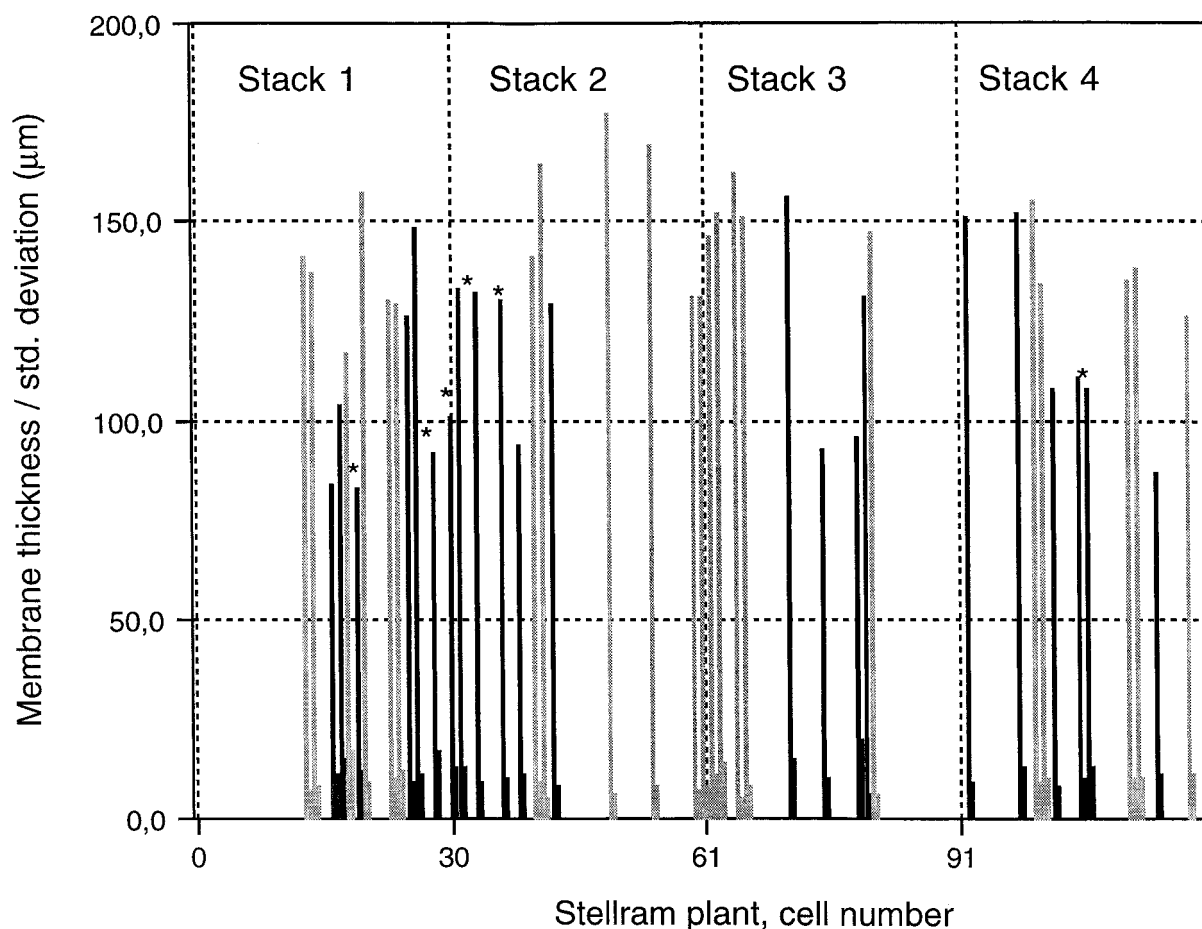


Fig. 2. Stellram plant: distribution of average membrane thickness along the electrolysis unit. Short bars at the bottom of the diagram show the standard deviation of the average thickness calculated from nine measuring points. Black bars refer to cells identified as having low voltage by the plant operators. Grey bars refer to cells chosen randomly. (*) Cells where membrane was found damaged (i.e., short circuit) after disassembly.

tions of the average values are also given (shorter bars on the right hand side of the bars indicating average thickness). The standard deviations tend to be larger for lower average thickness, indicating that membrane thinning is not occurring uniformly over the entire active area of a cell. As a reference, the thickness and standard deviation of a fresh Nafion® 117 membrane after standard hydration procedure was measured. The resulting average thickness was $229\ \mu\text{m}$, with a standard deviation of $7\ \mu\text{m}$.

The ion exchange capacity per unit of active area was determined for a number of membranes. For this, the actual active area of the membrane after disassembly and cleaning was determined and compared with the $400\ \text{cm}^2$ of active area in the electrolyser. The area specific ion exchange capacities given in Fig. 3 have been corrected to reflect the area in the electrolyser. The area specific ion exchange capacities correlate with the membrane thickness. The findings suggest that membrane degradation is not a process which is specific for the ion exchange groups of the polymer (i.e., preferential leaching of water soluble low EW polymer or preferential chemical attack on ionic groups).

5.2. Inspection and thickness analysis of membranes from SWB plant

The second demonstration unit of Membrel Technology on a 100 kW scale was operated by Solar Wasserstoff Bayern GmbH (SWB). The main purpose of this plant was to assess the suitability of the technology for the chemical storage of a variable solar electricity input. As a technology research facility the plant was monitored to much more detail than the Stellram unit. The plant was operated for only short periods and was in stand-by mode for most of the time. During stand-by periods, in order to avoid corrosion of the metallic parts of the cathode current collectors, a small protective polarization current of 150 mA, corresponding to $0.34\ \text{mA cm}^{-2}$, was applied to the cell modules at ambient temperature. This protective current was applied in all plants when the electrolyser was not in operating mode. The long stand-by periods were in most cases not due to availability problems of the Membrel system.

The reasons for shutting down and dismantling the plant were the same as in the case of the Stellram plant: gas purity problems (hydrogen levels in oxygen exceeding 3 vol %). In the case of the Stellram plant the final shut-down occurred after a total operating

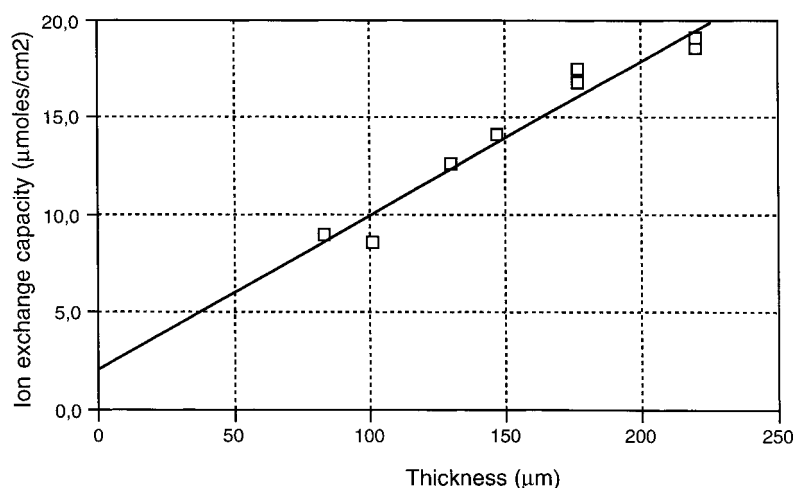


Fig. 3. Ion exchange capacity of membranes per unit electrode area for a number of cells from the Stellram unit. A (linear) relationship exists between area specific ion exchange capacity and thickness, suggesting unchanged equivalent weight in the remaining membrane material.

time of 15 000 h, while in the case of the SWB plant it occurred after a total operating time of 2300 h only. It must be stressed, however, that the SWB plant had been on stand-by for a total of 50 000 h. The gas purity record over the years before shut-down is given in Fig. 4. The hydrogen leakage to the anode compartment increased continuously over this period of time.

Deviations from normal in the cell voltages were recorded after four years. Cells 3 and 43 were first diagnosed short circuited (cell voltage zero under standby polarization conditions), followed by cells 5, 16 and 17 showing cell voltages below the thermodynamic water splitting potential (1.23 V) under stand-by conditions. After five years cells 1 to 20 and the cells in the upper part of the second module showed a significantly lowered cell voltage at stand-by. In the last stage, before disassembly of the stack, the voltages of the cells 1 to 30, 43, 46, 50 to 53 were found to be below normal.

The accumulation of faulty cells in the upper half of the electrolyser stack is confirmed by the thickness analysis of a sample of 30 membranes taken from the

disassembled electrolyser (Fig. 5). The thickness analysis was carried out using the automated measuring device described above. As in the Stellram case, all membranes which showed short circuit were included in the sample. Some areas of the membranes were still covered with carbon/PTFE particles from the cathode and some areas of the membrane were blistered. As a result, some of the thickness values exceeded markedly the reference thickness of a Nafion® 117 membrane. The thickness of the membranes in the area which was masked by the gaskets and had not been active electrochemically, was used as a reference. It averages for all membranes around 215 μm. Thickness values in the active area exceeding 220 μm (i.e., artefacts due to water blisters and/or incomplete removal of current collector material) on one hand, and lower than 30 μm (i.e., areas which had been damaged in operation or in process of dismantling) on the other were not considered for averaging the thickness data.

Figure 6 shows a plot visualizing the thickness profile over the whole area of membrane 3 (i.e., from the part of the electrolyser which was most

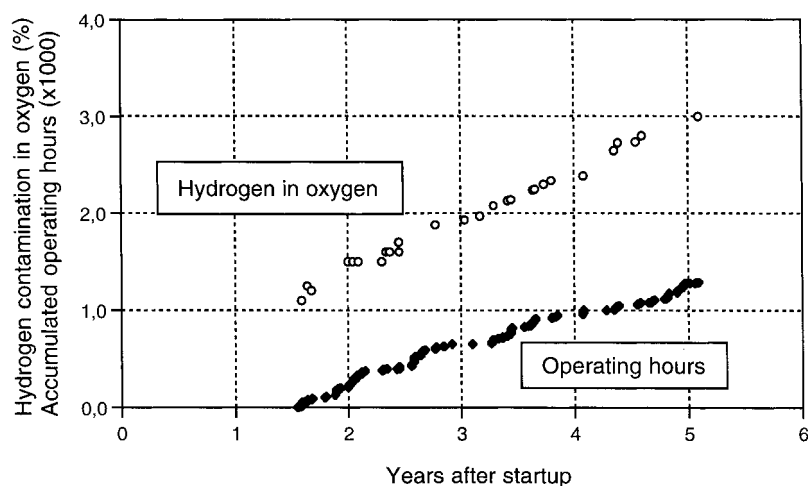


Fig. 4. Gas purity record as a function of lifetime of Membrel plant SWB. Open symbols: hydrogen content in anodic oxygen gas. Filled symbols: Accumulated hours during which the electrolyser was operating and producing gas.

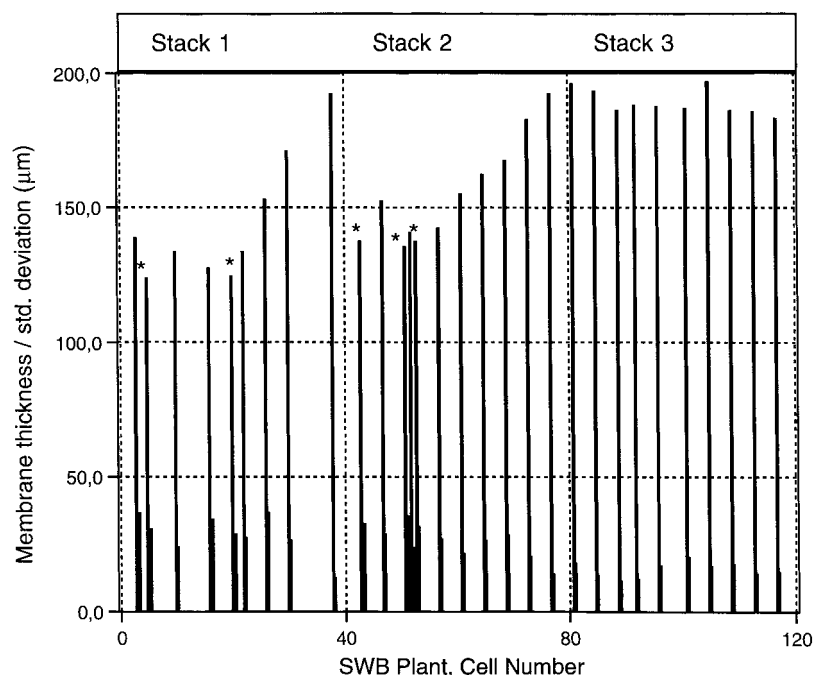


Fig. 5. SWB plant: Distribution of average membrane thickness in micrometre, along the electrolysis unit. (*) cells where membrane was found damaged (i.e., short circuit) after disassembly. Short bars at the bottom of the diagram show the standard deviation of the average thickness calculated from 24 measuring points.

affected by degradation). Thickness is clearly a function of position on the membrane. Practically all of the membranes from stack 1 and most from

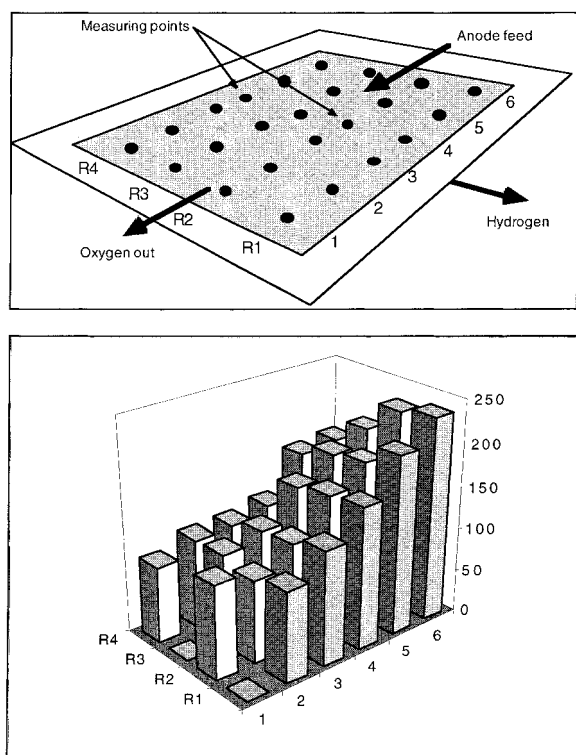


Fig. 6. (a) View on membrane as arranged for automatic measurement of the thickness distribution. Dots indicate measuring points on active area. Membrane is oriented such that anode face is up and cathode face is down. Direction of flows of water and products is indicated by arrows. (b) Local distribution of thickness for SWB-membrane no. 3. Column height represents the thickness recorded at the measuring dots. Membrane exhibits hot spots at the thin end (zero values).

stack 2 show the same general topography. Thinning and also the formation of hot spots is found predominantly near the one margin of the active area where the anodic product is leaving the cell. No thickness gradient along the membrane area is found in cells from stack 3. Figure 7 summarizes the findings of the thickness analysis with respect to position in the cell and in the electrolyser: it shows a plot of the average membrane thickness near the anode outlet channel (i.e., an average value calculated from the measuring points of row 1 in Fig. 6), as well as the average thickness near the inlet channel (i.e., the average value of the measuring points of row 6 in Fig. 6) for all the membranes analysed. This shows clearly that membrane thinning is a function of the position in the cell stack and along the membrane surface. No correlation between position of the cell in the electrolyser stacks and extent of membrane thinning was found in the case of the Stellram plant (see Fig. 2).

5.3. Laboratory experiments using multimembrane single cells

One set of experiments was carried out using an assembly of four Nafion® 117 membranes as solid electrolyte. This offered the possibility to separate interfacial and bulk degradation by investigating separately the membranes adjacent to the anode and the cathode, respectively, in a post mortem analysis.

Typical results of these experiments are shown in Fig. 8, where the amount of base consumption to neutralise the regenerated membrane acidity and the thickness of the four individual membranes are

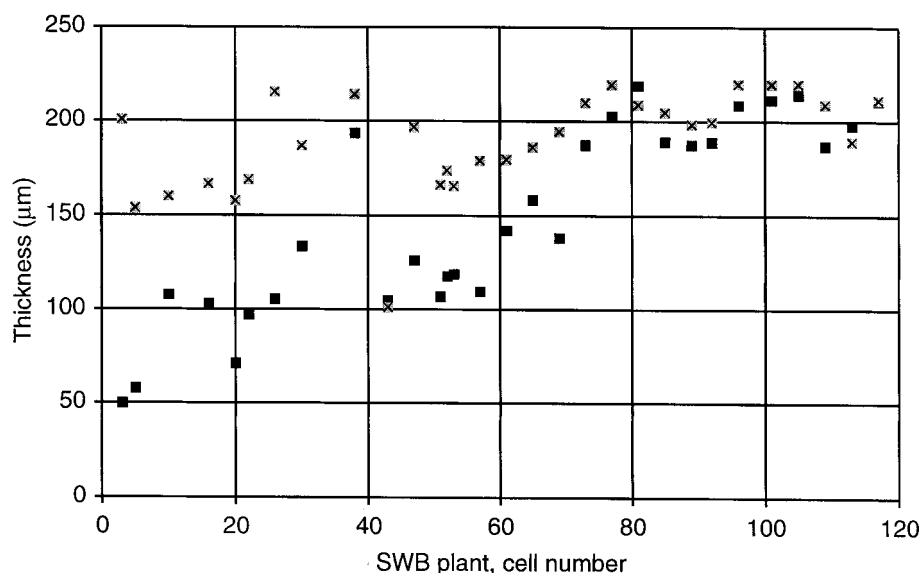


Fig. 7. Summary of membrane topography. (■) Average membrane thickness at the anode outlet side of individual membranes (i.e., from measurements in row 1 (cf. Fig. 6)); (x) average membrane thickness at the anode inlet side of individual membranes (i.e., from measurements in row 6 (cf. Fig. 6)).

plotted against their position in the cell. Clearly, only the base consumption and the thickness of the membrane adjacent to the cathode changed. Both values decreased in parallel, suggesting that the equivalent weight of the remaining membrane material remained constant. Surprisingly, this result of a heterogeneous degradation at the cathode (hydrogen side) parallels older results for membrane degradation in solid polymer electrolysis cells, however with membranes prepared from sulfonated *p*-styrene [12].

5.4. Operating experience with Membrel plant ATEL

The Membrel plant at ATEL has been in operation since 1991 and has accumulated a total of over 5500 operating hours. The state of the modules has been

checked periodically by measuring the cell voltages and monitoring the gas purities. As Fig. 9 reveals, the diagnostic parameters (i.e., oxygen purity and cell voltage) have levelled at constant values in the past two years. Accurate offline measurements of hydrogen levels in oxygen by gas chromatographic analysis have been available during the past two years. The periodic measurements of the cell voltages at nominal operating conditions (not available during the start-up phase of the electrolyser) reveal that none of the cells have developed significant deviations towards low cell voltages. The general trend in the average cell voltage is within the normal voltage increase due to catalyst ageing. The behaviour of the electrolyser so far does not indicate any signs of membrane failure, in contrast to the SWB plant (Fig. 4).

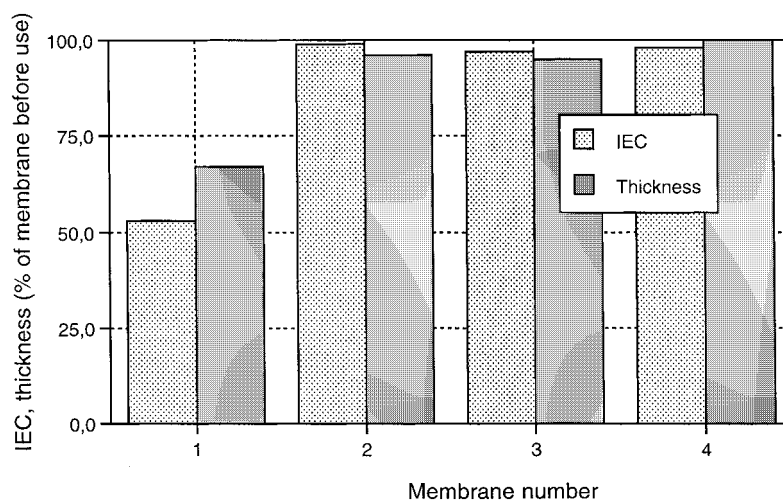


Fig. 8. Membrane thinning in a 30 cm² multimembrane laboratory cell: Membrane 1 was facing the cathode, membrane 4 was facing the anode. Ion exchange capacity and thickness of the membranes is given as a percentage of the corresponding values of membranes before use.

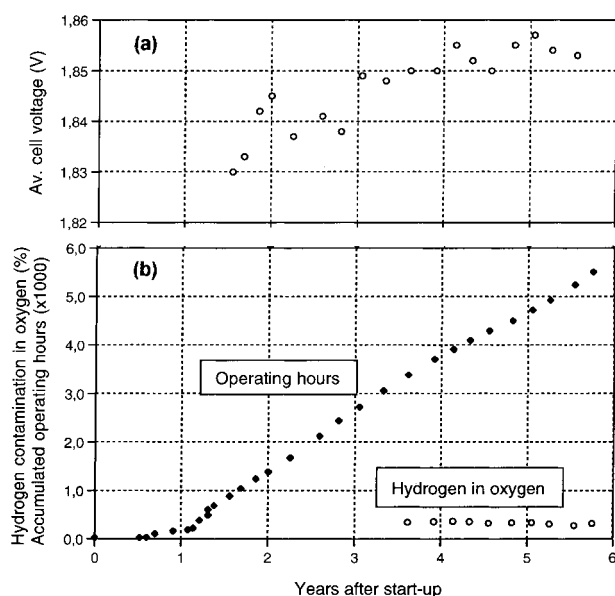
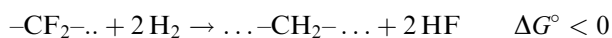


Fig. 9. Membrel plant ATEL: Average cell voltage of 120 cells operating at 10 kA/m^2 and 80°C (a), and gas purity record as a function of total plant lifetime, after revision in 1991 (b). Open symbols in (b): hydrogen content in anodic oxygen gas. Filled symbols: Accumulated hours during which the electrolyser has been operating and producing gas. Last record: May 1997; plant is still operating on a regular basis.

6. Discussion

Single PEM electrolysis cells with Nafion as the electrolyte membrane have reportedly been run with steady performance data over long periods of time ($> 20\,000 \text{ h}$) without detectable degradation [15]. On the other hand, the dimensional measurements carried out on the Nafion[®] 117 membranes after use in the 100 kW electrolysers show clearly that membrane material was lost during prolonged operation of the units. The ion exchange capacity measurements on thinned membranes reveal that the composition of the remaining polymer is not changed with respect to ionic groups (Figs 3 and 8). This rules out possible degradation mechanisms involving preferential attack on the ion exchange groups, which would manifest itself in an increased EW in the remaining polymer.

The experiments in small 30 cm^2 cells reveal that the membrane degrading reaction can be localised on the cathodic side of the cell and that the interface with the anode as well as the bulk of the membrane electrolyte are unaffected. Cathodic reduction of the C–F-bonds in the perfluorinated polymer is one of the thermodynamically possible steps which eventually may break up the polymer and lead to membrane failure:



A partial defluorination of the polymer material in the vicinity of the cathode would make the same more sensitive to attack by H_2O_2 , as postulated for membranes using nonperfluorinated polymers [12]. In order to quantify the extent to which the above reaction might contribute to the overall degradation, a careful

analysis of the permeated water in the cathode compartment of the electrolyser with respect to fluorides would have to be carried out. In fact, fluoride ions have been detected qualitatively in previous tests in laboratory cells, but no quantitative correlation of F-loads and membrane thinning has been made so far.

The results of the thickness analysis of the SWB membranes reveal that the thinning of the membranes in this particular case does depend on their position and orientation in the electrolyser stacks (cf. Figs 5 to 7). This finding strongly suggests that the extent of membrane degradation might depend on unaccounted parameters resulting from the design of the cells and/or stacks.

Inhomogeneities in current distribution with associated preferential membrane wear might result from uneven temperature distribution in the stack. Temperature effects at an average operating temperature of 80°C are, however, regarded to be relatively small (limited to 100°C by the boiling point of water).

The only stack design parameter we can think of to produce the systematic patterns observed in the membrane topography of the SWB electrolyser is uneven mechanical pressures exerted on the membrane by the clamping system employed. The obvious explanation for the influence of mechanical stress on membrane thickness would be creep of the membrane material. We have, however, strong evidence that the membrane thinning is due to effective material loss by a cathodic process and that mechanically induced creep can be excluded (Fig. 3). One possible hypothesis for explaining the observed membrane material loss is that mechanical stress on the membrane might enhance and/or trigger the corrosive process by local erosion of fragments of the membrane material by gas bubble nucleation. Bubble induced erosion would, however, also lead to degradation on the anodic side, which was not observed in the experiments with multimembrane cells (cf. Fig. 8). Any mechanically induced damage of the membrane by nucleating gas bubbles would depend on the pathways for gas evacuation from the membrane surfaces and hence on the pore structure of the current collectors employed. In the design of the Membrel electrolysers the pores in the anode current collectors have been made more open and hydrophilic than in the cathode current collectors which might explain the observed restriction of the effect to the cathode. To verify the hypothesis that gas bubble erosion at the cathode gives rise to the degradation of the membranes, the cathode water effluent from an electrolyser would have to be analysed for ionomer fragments (tensides).

We have, however, no experimental proof of the hypothesis (e.g., from long term measurements with laboratory cells with controlled mechanical stress on the membrane). The laboratory cells employed in the present study did not guarantee the control of mechanical parameters over the entire duration of an experiment (several thousand hours). The absence of any detectable membrane degradation so far in the

closely monitored plant at ATEL, and also the time to failure of the Stellram plant which was almost a factor of ten longer than the one of the SWB plant, are in favour of the hypothesis: in this design the pressure on the membranes is controlled by a hydraulic system which allows much better control of the homogeneity of the force applied to the active current bearing membrane.

7. Conclusions

The membrane is the weakest part in a PEM electrolyser regarding long term performance. Failure of 100 kW units using PEM technology has been due a process corroding or eroding the membrane material Nafion® 117. The dissolution process proceeds from the interface between the cathode and the membrane, is not specific with respect to the ion exchange groups, and is triggered and/or enhanced by local stress on the membrane. The effect of mechanical stress on the degradation process is plausible, however, more detailed studies to confirm this hypothesis would be necessary. The observed membrane degradation phenomena in industrial scale electrolyzers are a serious problem for the advancement of this technology and should be considered in further development work on technical PEM electrolyzers.

Acknowledgement

The authors thank Albert Schuler for his excellent technical assistance with cell disassembly and membrane thickness analysis.

References

- [1] R. Oberlin, M. Fischer, 'Status of the Membrel Process for Water Electrolysis', *Hydrogen Energy Progress VI*, vol.1, (1986) pp. 333–40.
- [2] W. T. Grubb, *US Pat. 2913 511* (1959).
- [3] G. G. Scherer, *Chem.-Ing. Tech.* **56** (1984) 538–9.
- [4] S. Stucki, G. Theis, R. Kötzi, H. Devantay and H. J. Christen, *J. Electrochem. Soc.* **132** (1985) 367.
- [5] W. G. Grot, *Chem. Ing. Techn.* **47** (1975) 617.
- [6] A. Eisenberg and H. Yeager, (Eds), 'Perfluorinated Ionomer Membranes', ACS Symposium Series 180, American Chemical Society, Washington DC (1982).
- [7] T. D. Gierke, G. E. Munn and F. C. Wilson, *J. Polym. Sci., Polym. Phys. Ed.* **19** (1981) 1687.
- [8] W. H. Hsu and T. D. Gierke, *J. Membr. Sci.* **13** (1983) 307.
- [9] J. Halim, F. N. Büchi, O. Haas, M. Stamm and G. G. Scherer, *Electrochim. Acta* **39** (1994) 1303.
- [10] M. H. Litt, Meeting Abstracts, Fall Meeting of the Electrochemical Society, San Antonio, Texas, 6–11 Oct. (1996), Vol. 96–2, p. 188.
- [11] F. N. Büchi, M. Wakizoe and S. Srinivasan, *J. Electrochem. Soc.* **143** (1996) 927.
- [12] A. B. LaConti, A. R. Fragala and J. R. Boyack, in 'Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage' (edited by J. D. E. McIntyre, S. Srinivasan and F. G. Will), The Electrochemical Society, Princeton, NJ (1977), p. 354.
- [13] H. Grüne, Ext. Abstract, Fuel Cell Seminar 1992, Tucson Arizona, pp. 161–3.
- [14] R. Kötzi, S. Stucki, *J. Appl. Electrochem.* **17** (1987) 1190.
- [15] G. G. Scherer, H. Devantay, R. Oberlin and S. Stucki, 'Wasserstoff- und Ozonerzeugung durch Membrel-Wasserelektrolyse', *Dechema Monographien*, **98** (1985) pp. 407–15.