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Nafion degradation in PEFCs from end plate iron contamination

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Abstract

Nafion degradation in polymer electrolyte fuel cells from SS316L end plate iron contamination was tested in a single cell configuration. Water collected at the cathode and anode exhausts was analysed by means of pH measurements, conductivity, fluoride and metal concentration. The investigations revealed that stainless steel is unsuitable as material for end plates in PEM fuel cells. In fact, iron contamination of membrane electrode assemblies led to polymer degradation, revealed by a massive fluoride loss. In contrast, iron-free plates (aluminium alloy) showed higher stability in the cell environment.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are very promising as energy source for electric vehicles thanks to their high power density performance at low temperature (70–90 °C). Nevertheless, the cost of a PEFC stack is still prohibitive for mass production and the introduction of low-cost materials and/or process is necessary. An effort is still needed to validate alternative materials suitable for use in fuel cell technology, which are able to achieve long lifetime of the overall system. The ultimate life of PEFCs is primarily related to the chemical stability of the membrane. Many parameters including fuel cell operation temperature, pressure and relative humidity of reactant gas may have significant effect on membrane life. For perfluorocarbon proton exchange membranes as Nafion, an accurate measure of the stability is the fluoride loss rate. Baldwin et al. [1] stated that mechanical failures are the main cause of fluoride loss. Liu et al. [2] agreed with this hypothesis, but also affirmed that local chemical or thermal degradations play a significant role on fluoride release. Besides, they concluded that more careful experimental design is needed to correlate F^- release with controlled parameters. In this work, a relation between iron

contamination from end plate materials and Nafion degradation in PEFCs was found. The requirements for end plate materials are sufficient mechanical strength and chemical stability in both oxidising and reducing conditions. These plates should also be cheap and well suited for high-volume manufacturing methods. High electrical conductivity is not relevant if end plates are not used as direct current collectors.

To our knowledge, no works have been addressed towards the evaluation of the metal contamination effect originating from end plates that are not in direct contact with the membrane electrode assembly (MEA). On the contrary, many references [3–10] cited metallic plates in direct contact with the MEA as a source of contamination. In fact, although at present the most commonly used bipolar plate is graphite, several authors are investigating alternative materials, for instance, pure metals and stainless steel with or without a protective and conductive coating. Furthermore, in all these works the effect of metal contamination on the Nafion properties was evaluated only in terms of ohmic loss caused by the entrance of cations and substitution of H^+ ions. Several authors [4,5,7,9,10] studied stainless steel 316L and their results can provide information on the behaviour of this material for use as end plates. Wind et al. [4] noted metal contamination in the MEA (single cell) using uncoated SS316L as current collector plates. Particularly, Cr, Fe and Ni contamination were detected

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in the MEA after the cell tests. The most important conclusion of this work [4] is that SS316L cannot be used directly in contact with electrodes because the metal contamination shortens the performance by increasing the membrane resistance. Moreover, the formation of oxide layers with high resistivity was also seen. Makkus et al. [5] concluded that stainless steel constituents slowly dissolved into the MEA and pointed that the anode side stainless plate was the main source of contaminants incorporated into the membrane/catalyst layer. The same work also stated that direct contact between stainless steel and the membrane greatly enhanced the contamination level. Cunningham et al. [10] showed that the decrease of performance was drastic for bare SS316L plates, which showed oxidation products on about 50% of their surface. Davies et al. [7] verified that uncoated SS316L presents low performance, but surprisingly they did not observe any evidence of corrosion for this material, which would cause poisoning of the membrane. The same authors [7] observed that stainless steel with increased Ni content should be preferred as material for PEFC production ($904L \geq 310 > 316$) in order to reach higher long-term stability, but they correlated this trend only to a lower interfacial resistance. Scholta et al. [9] suggested the avoidance of direct contact between ferrous alloys and the conducting ionomer and stated that SS316L was suitable for use as an intermediate layer avoiding a region in which the metal is in contact with water, but the same authors observed the need of extended long-term tests exceeding 1000 h.

In this paper, we investigated the influence of SS316L as a source of iron contamination by using this material as end plate without direct contact with the electrodes. Particularly, the influence of this contamination on Nafion degradation was studied. Commercial anticorrosional aluminium end plates were utilised for comparison and results showed a drastic reduction of Nafion degradation.

2. Experimental

2.1. Materials

Commercially available 20 wt.% Pt/C catalyst powders on carbon black (Vulcan XC72) were purchased from E-Tek Inc. Three-layer (substrate/diffusive layer/catalyst layer) gas diffusion anode and cathode (106 cm²) were prepared using a spray technique described in detail in previous works [11–13]. The substrate was carbon paper (Toray TGP090). The weight composition of the diffusion layer was 85 wt.% of carbon and 15 wt.% of PTFE, with carbon loading of 1.93 mg cm⁻². The catalyst layer was prepared by mixing appropriate amounts of carbon supported catalyst (24.5 wt.%), 5

wt.% Nafion ionomer solution from Aldrich (14.9 wt.%) and glycerol (60.5 wt.%). The platinum loading in all anodes and cathodes was kept constant at 0.34 mg cm⁻² on the MEA. Nafion 115 membrane (Du Pont) was used after purification treatment in 5 w/v% H₂O₂ solution at 80 °C for 1 h, followed by a second treatment in 1 M H₂SO₄. The MEAs were formed by hot pressing the electrodes (106 cm²) onto the membrane at 130 °C for 1–5 min and 50–100 kg cm⁻².

Membrane electrode gasket assembly (MEGA) technology [11] was used and a well-defined shape compatible with the cell hardware was achieved (Fig. 1). This technology allows to disassemble the cell and to replace the end plates, maintaining the same MEA [11]. In this work, SS316L and aluminium anticorrosional 100 (Alusuisse) end plates (185 × 185 × 11 mm³) were used. At the lateral borders of the assembly and end plates, manifolds holes for gas feeding are visible (Fig. 1). Graphite flow field plates were assembled with a typical parallel channel configuration using commercially available BMA5 graphite produced by SGL Carbon Group (Germany).

2.2. Physical–chemical characterisation

Full-cell electrochemical tests were carried out in the MEGA system using a 106 cm² single cell incorporated in a Globe Tech Inc. mod. 890 test station. Two SS316L end plates and two graphite flow field plates composed the single cell. After the measurements, the single cell was opened, the end plates were substituted by those made of aluminium and then the same MEGA was reassembled and tested again.

PEFCs were galvanostatically polarised with a programmable power supply interfaced with a computer for data acquisition. All measurements were carried out in the same operative conditions. Voltage was always measured directly onto copper thin sheets inserted between the end plates and graphite plates.

Water was collected periodically at the exhausts using plastic containers and stored for analysis. It must be emphasised that the cathode water (~ 50 cm³ day⁻¹) was the by-product of both the cell reaction and condensed humidification water, whereas the anode water was originated mostly from the anode side humidifier (~ 10 cm³ day⁻¹) and partially as diffusion water from the cathode side. pH measurements were conducted with an AMEL mod. 338 pH-meter. Water conductivity was measured by means of a Crison mod. 525 conductivity-meter. The fluoride amount released into the product water was determined using a Mettler Toledo F⁻ ion selective electrode. Metal contaminants were analysed by atomic absorption spectroscopy (AAS) with a Varian mod. SpectrAA 220 instrument.

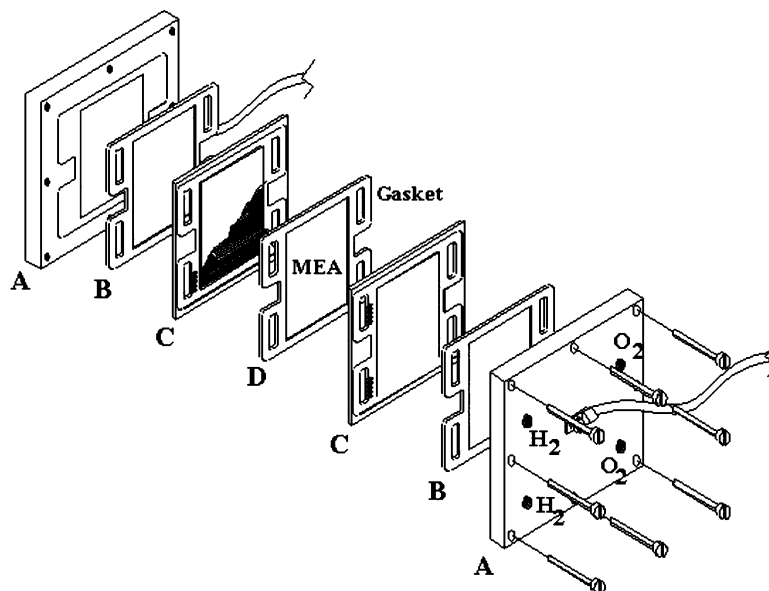


Fig. 1. Scheme of a single PEM fuel cell showing the location of the components: (A) aluminium or SS316L end plates, (B) copper current collector/gaskets, (C) graphite flow field plates, (D) MEA (MEA+Gasket). Hydrogen and oxygen inlet and outlet holes are shown.

3. Results and discussion

Long-term tests were carried out on the MEGA assembly at 25–70 °C and about 10–150 mA cm⁻² in H₂/O₂ flux. Fig. 2 shows current and temperature profiles for the tests. Both variables were changed daily and weekly. Temperature was changed from 50 °C (night) up to 70 °C in the mornings and was decreased to 25 °C during the weekends. The current density was varied from 9.4 mA cm⁻² (during nights and weekends) to 141 mA cm⁻². Fig. 3 shows the cell potential vs. time curve for a period of about 3 months. First, SS316L was tested as end plates and the average cell voltage was 0.76 ± 0.03 V, showing a slow decrease during time. In the following, aluminium end plates were mounted and the cell voltage was 0.78 ± 0.01 V, but the trend appeared to be stable. The difference in the calculated mean ohmic resistance (obtained from the voltage–current ratio) between the two materials was very low and it was difficult to attribute it to a well-defined

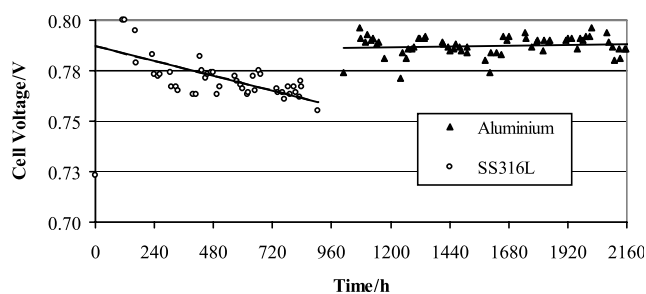


Fig. 3. Cell voltage vs. time for MEGA under H₂/O₂ flux 200 sec min⁻¹ 1.5/1.5 abs bar at 141 mA cm⁻².

phenomenon; we cannot exclude, however, the membrane contamination from metal ions (especially iron). As support, we can cite the work of St-Pierre et al. [3] who compared the performance of iron-free and 41% iron-contaminated MEAs and found a very low difference in ohmic resistance (~ 2 mΩ cm²).

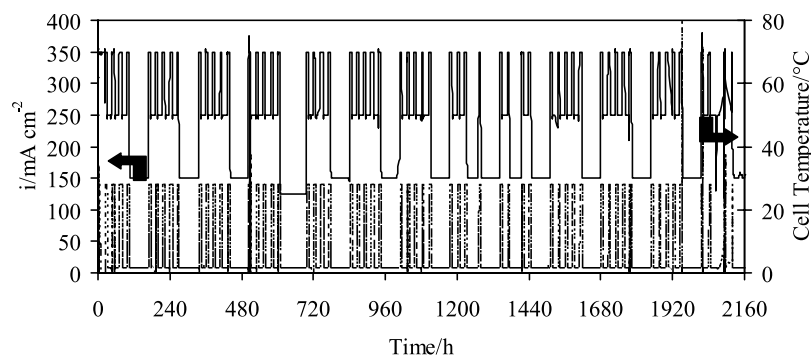


Fig. 2. Profiles of current density (dashed line) and cell temperature (solid line) vs. time for MEGA under H₂/O₂ flux 200 sec min⁻¹ and 1.5/1.5 abs bar.

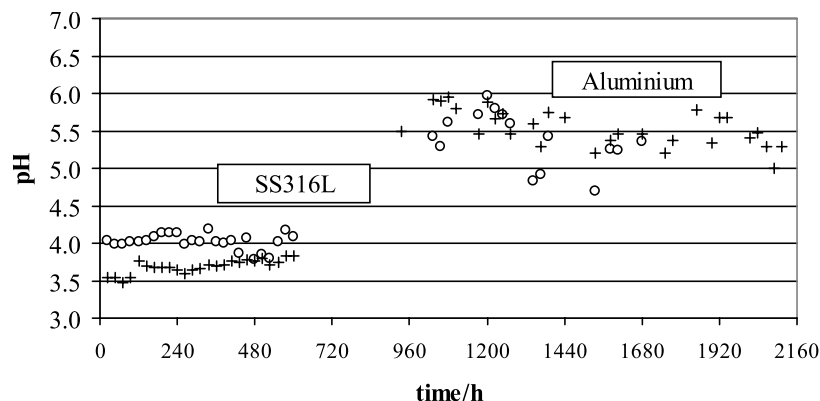


Fig. 4. pH vs. time for anode (+) and cathode (O) water for SS316L and aluminium.

However, the pH analysis of the water collected at the cathode and anode brought about some relevant evidences. Fig. 4 shows the pH values of the water collected at the cathode and anode. By using the SS316L end plates, the average pHs for the cathode and anode water were 3.7 and 4.1, respectively. The trend for both curves showed a pH decrease for the anode and an increase for the cathode up to an intersection point of about 3.9. We can suppose the existence of a correlation between these two pH variations up to when a steady-state condition is reached. Anyway, this pH is significantly lower than the expected value for water at the fuel cell outlet, which should be similar to that of pure water in the presence of dissolved CO_2 (pH ~ 5.7 for Milli-QTM water left in air for 1 h). In contrast, by mounting the aluminium end plates, the pH increased to 5.5 for the cathode and 5.4 for the anode, agreeing with the value cited above for pure water.

The anomalous release of H^+ cations can be justified only in the presence of anions to guarantee the charge neutrality in water. In our case, we have found a correlation between the presence of fluoride anions in the collected water and the H^+ concentration, as illustrated in Fig. 5.

The analysis of fluoride release at the cathode side as a function of time (Fig. 6) using the two different

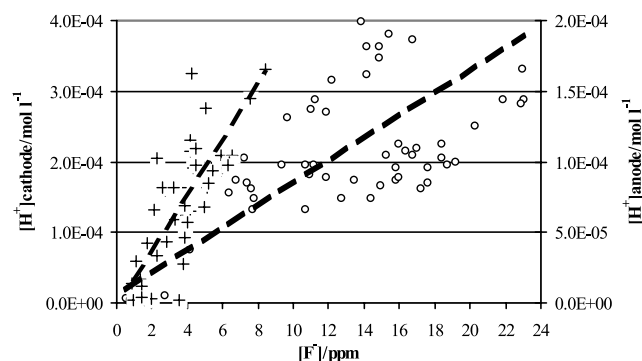


Fig. 5. $[\text{H}^+]$ anode (+) and cathode (O) vs. fluoride concentration in the collected water.

materials revealed a significant difference. The average F^- concentration using SS316L was 14 ppm with a standard deviation of ± 5 . In contrast, the average F^- concentration and the conductivity decreased 12 times by changing the end plate material. In fact, also the conductivity measurements can be a fast and efficient method to control this anomalous behaviour. A good linear correlation between fluoride ion concentration and conductivity can be seen in the insert of Fig. 6. This is not surprising considering that the conductivity depends mainly on H^+ ions.

Table 1 summarises the average pH, conductivity and fluoride concentration values obtained for anode and cathode using the two different materials. It was evident that fluoride release (and conductivity) varied much more significantly at the cathode side and, considering that water production occurs only at this side, it is difficult to evaluate if the anode results depend mainly on the water diffusion from the cathode into the anode. In this sense, we have considered only the cathode results.

As mentioned above, some literature data [4,5,14] revealed that SS316L, if used as bipolar plate in a PEFC environment, releases metal ion contaminants. In our case, the end plates were not in direct contact with the graphite backing layer or membrane and the only surfaces that could be a source of contaminants, once they were exposed to H_2 , O_2 and humidification water, were the gas inlet and outlet holes machined into the end plates (Fig. 1). The exposed metal area for each inlet and outlet hole was 7.74 cm^2 . To verify the presence of these metals, AAS analysis was performed on cathode water. As we supposed, the results in Fig. 7 show that SS316L was the source of contaminants and by removing this material a reduction of 15–22 times in contamination occurred. The metal amounts of the cathode water followed the same trend of the SS316L elemental composition ($\text{Fe}^0 \gg \text{Cr}^0 > \text{Ni}^0$). Considering a daily working time of about 6.5 h, the average contaminant production rates were 94, 18 and $14 \mu\text{g h}^{-1}$ for Fe, Cr and Ni, respectively. These rates are comparable with

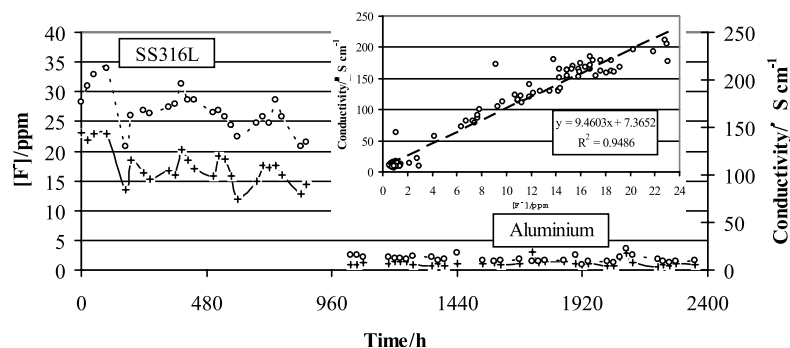


Fig. 6. Fluoride concentration (+) and conductivity (O) vs. time in the cathode water for SS316L and aluminium. The insert shows the linear correlation between fluoride concentration and conductivity.

Table 1
Average pH, fluoride concentration and conductivity during time tests

	pH		[F ⁻]/ppm		Conductivity/μS cm ⁻²	
	SS316L	Al	SS316L	Al	SS316L	Al
Cathode	3.7	5.5	14	1.2	143	12
Anode	4.1	5.4	4	1.6	82	15

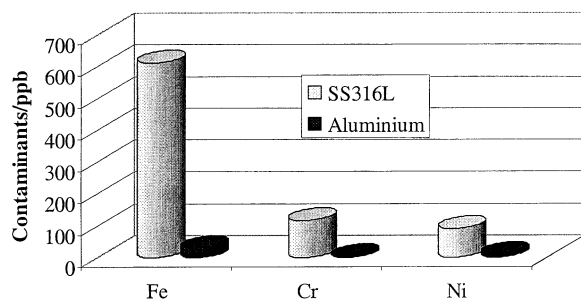


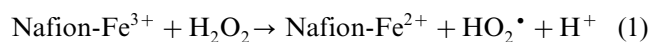
Fig. 7. Average contaminant concentration in the cathode water using SS316L or aluminium end plates.

those obtained by Wind et al. [4] analysing the MEA after 100-h cell test especially for Ni^{2+} . Okada et al. [14] observed a density increase and a shrinkage effect if these multivalent cations are exchanged for H^+ in the membrane. Besides, these cations have a high preference over H^+ in Nafion sulphonic group following the trend $\text{Fe}^{3+} > \text{Ni}^{2+}$.

The following question might arise: is there a correlation among the observed phenomena, i.e., metal contamination, pH increase and simultaneous F^- release? We can discuss this problem considering the following authors. It is known that the C–F bond in the polymer chain is poorly reactive [15] but, as reported by Baldwin et al. [1] and Liu et al. [2], fluoride release occurring on Nafion should predict its durability. Baldwin et al. [1] reported a life prediction of 10000 h for a fluoride release rate of $5.38 \times 10^{-8} \text{ g F}^- \text{ cm}^{-2} \text{ h}^{-1}$ and 4000 h for $2.47 \times 10^{-7} \text{ g F}^- \text{ cm}^{-2} \text{ h}^{-1}$ for a Nafion membrane with thickness of 200–250 μm working at 0.5 A cm². Liu

et al. [2] measured the fluoride loss for Nafion 101, but found difficulties in reproducibility and did not note any particular trend. The same author reported a fluoride loss rate in the range 3×10^{-7} to $4 \times 10^{-7} \text{ g F}^- \text{ cm}^{-2} \text{ h}^{-1}$ after 200 h of cell working. These values, transferred to Baldwin's expected lifetime plot [1] normalised for different thicknesses, furnished a cell life of about 1928–3101 h. This prediction is acceptable, considering the very thin membrane thickness (25 μm) used by Liu et al. [2]. In our case, we calculated an average fluoride loss rate of about $1.04 \times 10^{-6} \text{ g F}^- \text{ cm}^{-2} \text{ h}^{-1}$ using SS316L and $8.8 \times 10^{-8} \text{ g F}^- \text{ cm}^{-2} \text{ h}^{-1}$ with aluminium, corresponding to a lifetime increase of approximately 12 times. It is worth pointing that, in our case, fluoride release can occur due to the degradation of the membrane and/or Nafion ionomer in the electrode catalytic layer, so our calculated lifetime increase must be referred to all Nafion polymer present.

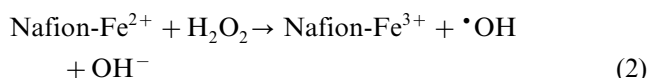
It is not so straightforward to explain the role paid by the metal ions on this phenomenon. However, in agreement with Turner's work [16], we can outline that especially Fe ions acts as catalyst-like agents in the Nafion degradation. As support to this hypothesis, we mention the works of Balanosky et al. [17] and Maletzky et al. [18] who reported that, under defined conditions, immobilisation of iron ions (Fe^{3+}) on Nafion sulphonic groups is a method to perform degradable oxidation of organic compounds by means of hydroxyl radical production. Their method, utilised in wastewater treatment, is based on a modification of the classical Fenton's reaction [19] and is able to oxidise organic compounds. Briefly, the Fe^{3+} ions immobilised on Nafion in the presence of peroxide can produce radicals by reduction into Fe^{2+} [18]:



In our case, the peroxide presence can be easily assured as product of oxygen reduction reaction on platinum, as reported by Yeager [20] ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$). The amount of H_2O_2 was related with the presence of halogen anions such as bromide [21] and chloride [22]. Schmidt et al. reported [22] that in acidic

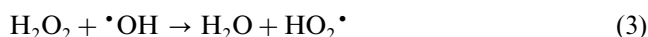
medium the peroxide production on Pt/C in the presence of Cl^- (10^{-4} to 10^{-3} M) was in the molar fraction range 2–8% at the electrode potential of approximately 0.7–0.8 V vs. RHE, which is close to our working potential (Fig. 3). These chloride impurities on the level of some parts per million can be easily obtained either by incorporation into the MEA during preparation or by contamination of the humidified fuel cell feed streams. Besides, on the basis of these results, we can hypothesise the same effect on H_2O_2 production, occurring in the case of F^- presence.

On the other hand, the modified Fenton's reaction [18] (Eq. (1)) requires the continuous oxidation of Fe^{2+} to Fe^{3+} but, in our case, Fe^{3+} could be continuously provided by the SS316L oxidation and, however, the $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ inverse reaction should be spontaneous at the cathode. Anyway, also Fe^{2+} can react with peroxide (Eq. (2)) producing the hydroxyl radical [18]:



The hydroxyl radical is one of the most reactive chemical species known and, in long time, can degrade Nafion polymer chains consequently increasing the fluoride loss.

The propagation step would be hindered by an excess of H_2O_2 acting as an $\cdot\text{OH}$ radical scavenger in solution (Eq. (3)).



It is important to point that the H_2O_2 and Fe concentrations necessary to the Fenton's reaction can be very low (e.g. $< 10\text{--}25 \text{ mg l}^{-1} \text{ H}_2\text{O}_2$). Typical ranges are 1 part Fe per 5–25 parts H_2O_2 (w/w) [18,19]. The optimal pH for the above reactions is between 3 and 6 and well fits with our operative conditions.

Based on the hypothesis outlined above, we can justify the decrease of membrane lifetime caused by the massive fluoride release caused by iron contamination. As support to our hypothesis, experimental data (Fig. 8) showed a significant linear relation between the Fe and F^- concentrations in the cathode water. On the opposite, no relations were found for Cr and Ni.

As already stated, although the anodic results might depend on water diffusion across the membrane from

the cathode into the anode, we can suppose that the modified Fenton's degradation mechanism acts partially also at the anode side. The analysis of the average Fe concentration in the anode water produced approximately 925 ppb, corresponding to a corrosion rate of approximately $142 \mu\text{g h}^{-1}$. This value was in agreement with Makkus' observation that the anode side stainless plate was the main source of contaminants [5]. Though this value was about 35% higher than the cathode corrosion rate ($94 \mu\text{g h}^{-1}$), the fluoride release at the anode, was found to be much lower (Table 1). This could be a consequence of a lower production of hydroxyl radicals at the anode side (Eqs. (1) and (2)) due to an insufficient contribution of peroxide. In fact, only small amounts of O_2 reaching the anode side for membrane crossover could produce H_2O_2 , as justified by Schmidt et al. [22] for typical anode potentials.

It is important to emphasise that in Refs. [17] and [18] no direct degradation of perfluorosulphonic membrane in the Nafion/Fe^{2+} to $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system was observed. Nevertheless, these measurements were performed only in very short times (from hundreds of minutes to some hours) and the degradation was studied only in terms of wastewater process efficiency, whereas the fluoride release was not taken into account. It has been shown above, however, that the F^- loss can influence the Nafion stability only after thousands of hours.

4. Conclusions

In this paper, the effect of metal contamination from SS316L was investigated. Some considerations can be outlined:

- metal contamination originated mainly from the anode side;
- increase of water acidity and conductivity at both the anode and cathode, especially the last;
- fluoride release mainly at the cathode side from polymer in the catalyst layer and/or membrane as a function of metal ion contamination, especially Fe.

A modification of the classical Fenton's reaction mechanism was proposed to explain the fluoride release especially in the cathode water. Further investigations are needed to better understand this effect. However, the correlation between the fluoride loss rate and Fe metal ion contamination from end plates suggests the avoidance of materials releasing this element in all parts of the fuel cell system in contact with humidified oxygen and hydrogen, i.e., bipolar plates, end plates, connections, tubes and tanks. Amongst the stainless steel types, those with lower Fe content (e.g. SS904L, SS310) should be

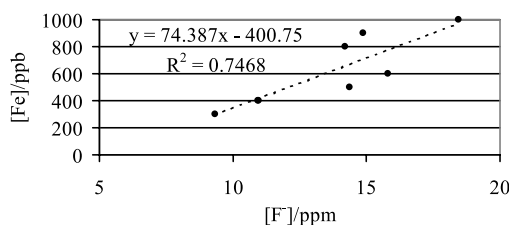


Fig. 8. Iron concentration vs. fluoride release in the cathode water using SS316L end plates.

preferred. In our case, the use of iron-free materials shows to be much more suitable in a fuel cell system.

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