Type of the Paper (Article)

Assessing the ageing process of cation exchange membranes in bioelectrochemical systems

M. Isabel San-Martín[1], Francisco Javier Carmona[2], Pedro Prádanos[3], Antonio Morán[1], Adrián Escapa[1,4,*].

[1] Chemical and Environmental Bioprocess Engineering Group, Natural Resources Institute (IRENA), Universidad de León, Avda. de Portugal 41, 24009, León; Spain amorp@unileon.es

[2] Dpto. de Física Aplicada. Escuela Politécnica, Universidad de Extremadura, 10004 Cáceres, Spain; jcarmona@unex.es

[3] Grupo de Superficies y Materiales Porosos, Dpto. Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, 47071, Valladolid, Spain; pradanos@termo.uva.es

[4] Department of Electrical Engineering and Automatic Systems, Universidad de León, Campus de Vegazana s/n, 24071 León, Spain

* Correspondence: adrian.escapa@unileon.es e-mail@e-mail.com; Tel.: +34 987295394

Abstract: Bioelectrochemical systems (BES) encompass a group of biobased technologies capable of directly converting organic matter into electricity. In these systems, which are derived from conventional electrochemical technologies, the ion exchange membrane represents a key element because of its influence on the economic feasibility and on the performance of BES. This study examines the impact of long-term operation of a BES on the mechanical, chemical and electrochemical properties of five different kind of cation exchange membranes (Nafion-117, CMI-7001, Zirfon UTP 500, FKE and FKB) through several techniques: (i) scanning electron microscopy (SEM) and atomic force microscopy (AFM) to assess the changes on the membranes surface, (ii) thermogravimetric analysis (TGA) to evaluate the structural stability of the membranes, and (iii) ion exchange capacity (IEC) to monitor any change in their electrochemical properties. Results confirmed that there is not an ideal membrane for BES. While Nafion and CMI-7000 exhibited the strongest chemical structure, they also underwent the highest fouling as revealed by a fast increase in surface roughness.

Keywords: Bioelectrochemical system; Cation exchange membranes; Ageing of membranes; Microbial electrolysis cell.

1. Introduction

During the past 15 years, bioelectrochemical systems (BES) have experienced an intense phase of research and development, proving to be a versatile group of technologies with a wide range of potential applications (e.g.: energy recovery from organic matter, chemical production from carbon dioxide, nutrient recovery from waste streams, etc.) [1]. BES are also capable of dealing with a broad range of organic and inorganic substrates [2] which gives them a great operational flexibility. Despite that, and despite the numerous scale-up experiences reported in the literature [3], BES are far from being a mature technology [4]. The still low current densities, relatively large capital cost and the difficulties associated with energy harvesting/management are often cited as major challenges in their way towards practical application [3].

The ion exchange membrane (IEM), which is a core element in BESs, has a significant impact on both the performance [5] (eg.: coulombic efficiencies and internal electrical resistance) and the capital costs [4], being responsible for up to 40% of the overall cost of BES [6]. Thus, it is not surprising that, in an effort to improve the commercial perspectives of BES, many researchers have come up with alternative designs that completely dispense with the membrane. Although many of them have proved to be successful in several fields of application such as organic and inorganic contamination removal [7,8] or energy production [9], the IEM becomes a critical element when the aim is to

optimize energy efficiency (by avoiding oxygen and hydrogen crossover [4,6]) or accomplish processes of industrial interest (nutrients recovery, microbial electrosynthesis or seawater desalination [10]). The application of several types of IEM such as anion exchange membranes (AEM), cation exchange membranes (CEM), microfiltration membrane, bipolar membrane and ultrafiltration membranes to BES has been extensively covered in the literature [6]. Nafion has remained the most popular because of its good mechanical stability and high proton selectivity [11], although its high price has motivated the search for other cheaper alternatives, such as Fumasep, Ultrex, Zirfon or Hyflon [12].

Ideally, a membrane apt for BES use should have low electrical resistance (to facilitate the ion transport), should prevent gas and substrates diffusion, have a high biofouling resistance, and all of this, preferably, with low-cost [13]. The membrane degradation, commonly known as 'membrane ageing', is another important aspect as it is directly related to their durability. Membrane ageing is usually characterised in terms of physical, chemical and electrochemical stability and to this end, a vast array of methods is available including microscopy, impedance spectroscopy or titration technics. Previous studies have made use of these techniques to investigate the ageing of individual membranes [10, 11], but there is a lack of knowledge on how these membranes compare in terms of their ageing patters a stability. In this study, we aim at filling this gap by assessing how the mechanical, chemical and electrochemical properties of five commercially available cation exchange membranes develop during four months of continuous operation within the environment of a microbial electrolysis cell (MEC). All the membranes were subjected to identical operational conditions by being fitted within the same MEC reactor. Membranes samples were collected on a monthly basis. Sscanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to assess the changes on the membranes surface; thermogravimetric analysis (TGA) to evaluate the structural stability of the membranes, and ion exchange capacity (IEC) to monitor any change in their electrochemical properties.

2. Materials and Methods

2.1. Microbial electrolysis cell design and operation

This work assesses the ageing process of five commercially available CEM (see section 2.2 for a complete description of them). To make sure that all membranes were subjected to the same operational conditions (i.e.: same pH, temperature, hydraulic retention time, etc) they were arranged within the same MEC reactor by using the frame shown in Figure 1. This frame consisted of two identical methacrylate plates with 30 windows (30 mm x 12 mm) opened in the plates to accommodate the membranes samples (6 for each type of CEM tested). The two plates were joined by small screws to facilitate the sampling process which was carried out on a monthly basis (see section 2.2).

The anodic and the cathodic chambers were constructed with methacrylate plates too and were separated by the frame above described. Each chamber retained 230 mL of liquid and had a headspace of 20 mL. The anode was made of a 5 mm-thick graphite felt (Sigratherm®, Germany), and the cathode consisted of a stainless steel mesh, both measuring 24.5 cm x 9.5 cm. The carbon felt was pre-treated with a method listed elsewhere [16] and the stainless steel was cleaned with distilled water. A titanium wire was used as current collector to connect the electrodes to a power supply PS2000B (Elektro-Automatik, Germany). The applied voltage was set at 1 V between anode and cathode and the electrical current was recorded every 10 minutes across an 8 Ω resistor by means of a 2700 Keithley multimeter (Keithley Instruments, USA).

The anode chamber was inoculated with a mixture activated sludge andeffluent from another MEC operated for 4 months. The anolyte stock solution was composed 0.55 g·L^{-1} sodium acetate, 6 g·L^{-1} K$_2$HPO$_4$, 3 g·L^{-1} KH$_2$PO$_4$, 1.5 g·L^{-1} NH$_4$Cl, 1 g·L^{-1} NaHCO$_3$, 0.5 g·L^{-1} NaCl, 0.2 mg·L^{-1} CaCl$_2$, 0.15 g·L^{-1} MgSO$_4$·7H$_2$O and 1 mL·L^{-1} of a mixed trace element solution and vitamins [17]. The catholyte stock solution consisted of a 0.1 M phosphate buffer. Both were sparged with nitrogen gas for 20 minutes to ensure anaerobic conditions and stored at 4ºC until use. Anolite and catholyte were feed

in continuous mode by means of two peristaltic pumps at a flow rate of 30 mL·h⁻¹, thus providing a 7 h retention time.
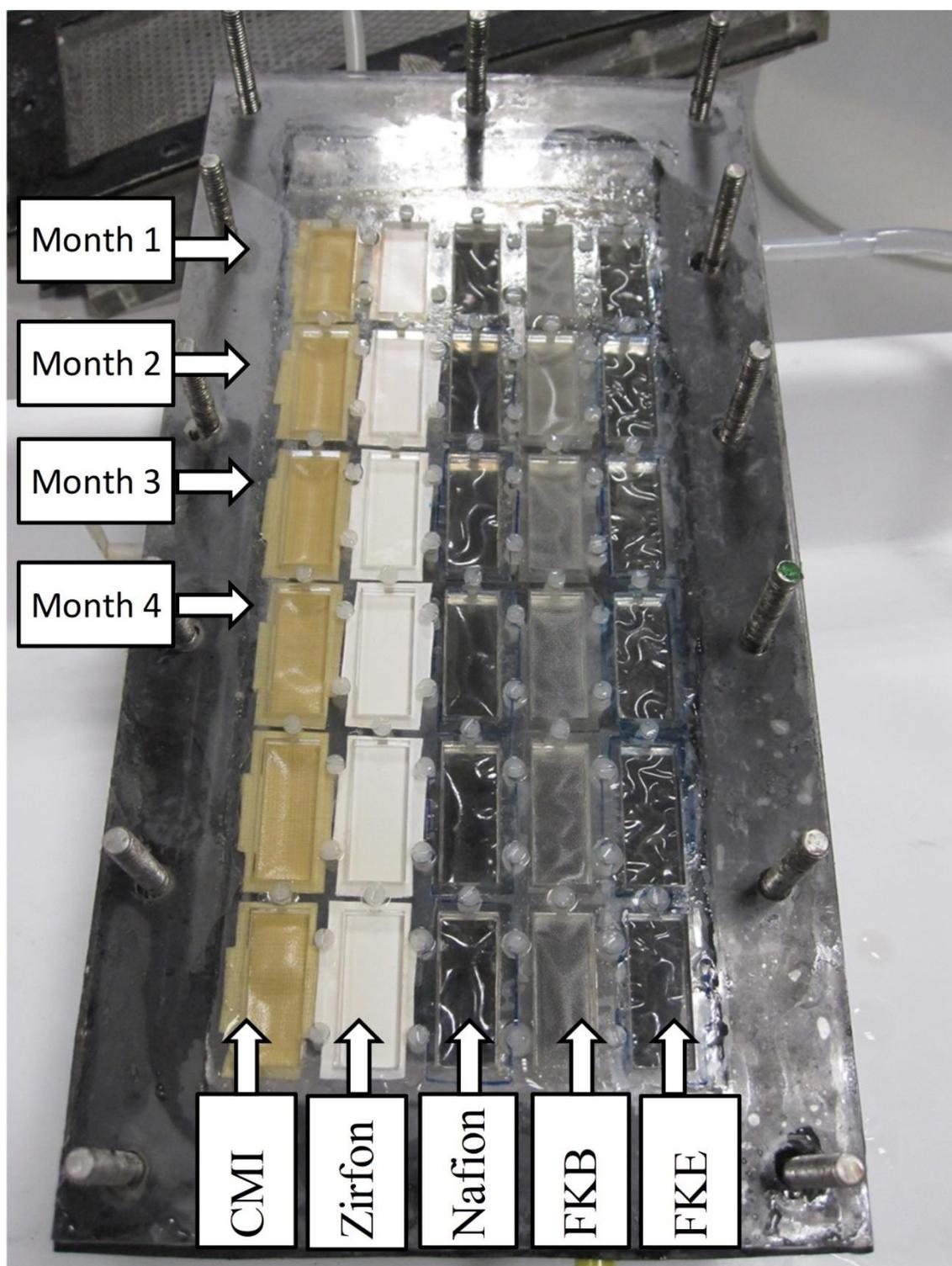

Figure 1. The methacrylate frame housing the 6x5 CEM membrane's samples

2.2. Membranes and membranes characterisation

Five commercially available CEM were used: Nafion 117 (DuPont, USA), CMI-7000 (Membranes International, USA), Zirfon Perl UTP 500 (Agfa, Belgium), Fumasep FKE and FKB (Fumatech, Germany). Table 1 shows some of their characteristics as provided by the manufacturer. After being

placed in the frame (Figure 1), the 5x6 membrane samples were soaked in demineralised water for at least 24 h.

Table 1. Physical and chemical properties of the cation exchange membranes used in this research

Property	Units	FKE	FKB	Nafion 117	Zirfon UTP 500	CMI-7000
Selectivity	%	> 0.98	> 0.98	-	-	> 0.97
Electric resistance	$\Omega \cdot cm2$	< 3	< 4	1.5	< 0.3	< 30
Stability	pH	1-14	1-14	-	6 M KOH	1-10
Thickness	mm	0.05-0.07	0.08-0.1	0.18	0.5	0.45
Ion exchange capacity	meq/q	>1	0.9-1.0	0.95-1.01	-	1.6
Cost	€/m2	195	320	400	45	170

The ageing process of the five membranes was assessed on samples taken after 1, 2, 3 and 4 months of operation (Figure 1). After sampling, a fresh membrane was placed in the vacant window, the MEC was reassembled and both chambers were purged with nitrogen gas. Although the initial plan for the experiment was to continue the sampling process for 6 moths (hence the 6 samples for each type of membrane in the frame), it was stopped at month 4 because the ageing tended to stabilize after the first month of operation of the MEC. The ageing of the membranes was evaluated according to the observed changes in their (i) superficial morphology (analysed by scanning electron microscopy and atomic force microscopy), (ii) structural stability (measured by thermogravimetric analysis), (iii) number of fixed charges inside the cation exchange membrane (measured according to the ion exchange capacity) and (iv) electrical resistance (calculated by electrical impedance spectroscopy). All these techniques are described in the following sections.

2.3. Scanning electron microscopy (SEM)

A JSM-6480 LV (JEOL, Japan) scanning electron microscope was used. The samples were fixed in a 2.5% glutaraldehyde solution in phosphate buffered saline (PBS) solution for 2 hours at 4° C. After drying the membranes with ethanol, they were transferred into the chamber of a critical point dryer CPD 030 (Bal-Tec, Germany). Subsequently, prior to observation of the microstructure by SEM, the membranes were coated with a thin layer of gold in a sputter coater equipment EM ACE200 (Leica Microsystems, Switzerland).

2.4. Atomic force microscopy (AFM)

A Nanoscope Multimode IIIa scanning probe microscope from Digital Instruments (Veeco Metrology Inc., USA) was used, following the method described elsewhere [18]. The calculated values of surface roughness were averaged over 5 different profiles for each membrane sample using a scanning area of 1×1 μm^2. The AFM allows to monitor changes on the membrane surface and get a quantitative measurement of roughness as Sq [19]. Sq refers to the root mean square roughness and represents the statistical measure of the magnitude of the height distribution. It was calculated according to Eq. 1:

$$S_q = \sqrt{\frac{1}{mn}\sum_{i=1}^{m}\sum_{j=1}^{n} Z^2(x_i, y_j)} \ , \tag{1}$$

where *m* and *n* are the number of the pixels in the x and y directions respectively (512×512 in this case), and *Z* is the height of a pixel.

2.5. Thermogravimetric analysis (TGA)

The thermogravimetric analyses were carried out with a Thermogravimetric Analyzer SDT Q600 (TA Instruments, USA), in a temperature range from 30 to 750 °C, at the constant rate heating of 10 °C·min^{-1}, under the nitrogen atmosphere.

2.6. Ion exchange capacity (IEC)

The ion exchange capacity was determined by acid-base titration. Initially the membranes samples were immersed in distilled water and soaked in a large volume of 1 M HCl solution for at least 24 hours (the solution was replaced three times to complete the ion exchange). After that, they were washed again with distilled water to remove the excess of HCl and soaked in a 2 M NaCl solution for at least 24 hours to replace the protons by sodium ions (again, the solution was replaced three times to ensure a complete exchange). The different NaCl solutions were collected and then titrated with 0.1 M NaOH. The ion exchange capacity titration of the membrane was calculated as the ratio between the total charge (meq) and the dry weight of the measured membrane (g).

3. Results and discussion

As described in section 2.2, the ageing of the five membranes considered in this study was assessed according to modification in their surfaces, structural stability and ionic exchange capacity. In the following paragraphs, these properties are described and discussed in detail.

3.1. Assessment of membrane surface modifications through SEM and AFM

Cation exchange membranes are liable to undergo biological and chemical fouling when operated in BESs [20]. The interest in tracking this phenomenon lays in the fact that fouling represents a physical blockage to charge transport through the membrane, which can result in a decay of current [20]. Although there is no specific procedure to measure its formation rates, SEM can provide a qualitative estimation of its physical extent [6]. As it can be observed in Figure 2, SEM analyses did not reveal any visible difference between fresh (unused) membranes and those samples taken after 1 and 4 months of operation. No biofouling was perceptible on either the anode nor on the cathode side and no breakings or deformities in the internal structure of the membranes were detected at a 90x magnification.

Still, these results need to be interpreted with caution precisely because of their qualitative nature. The apparent lack of any of surface deterioration might be hiding inorganic salts precipitations, biomass and extracellular polymers that are not easily perceptible on the SEM images and that may be depositing on the membranes surfaces [20]. Here, monitoring the evolution of surface roughness through AFM analyses and computed by the root mean square roughness (Sq, see section 2.4) can provide an indirect and quantitative evidence of fouling (any change on Sq in membranes exposed to bioreactors indicates that foulants are deposited [21]). Figure 3 shows how Sq increases more visibly in CMI and Nafion membranes (especially after the first month of operation). The Zirfon membrane, despite displaying the highest surface roughness on the fresh sample (probably because of the presence of ZrO$_2$), developed the least relative increase over the four months of operation which might be indicative of low fouling (Figure A1, Appendix A). This is indeed a surprising result, as membranes with high initial surface roughness tend to promote biofouling more easily [22], which clearly contrasts with our results. The roughness of FKB and FKE membranes increased progressively along the four months but always kept below the other three membranes studied.
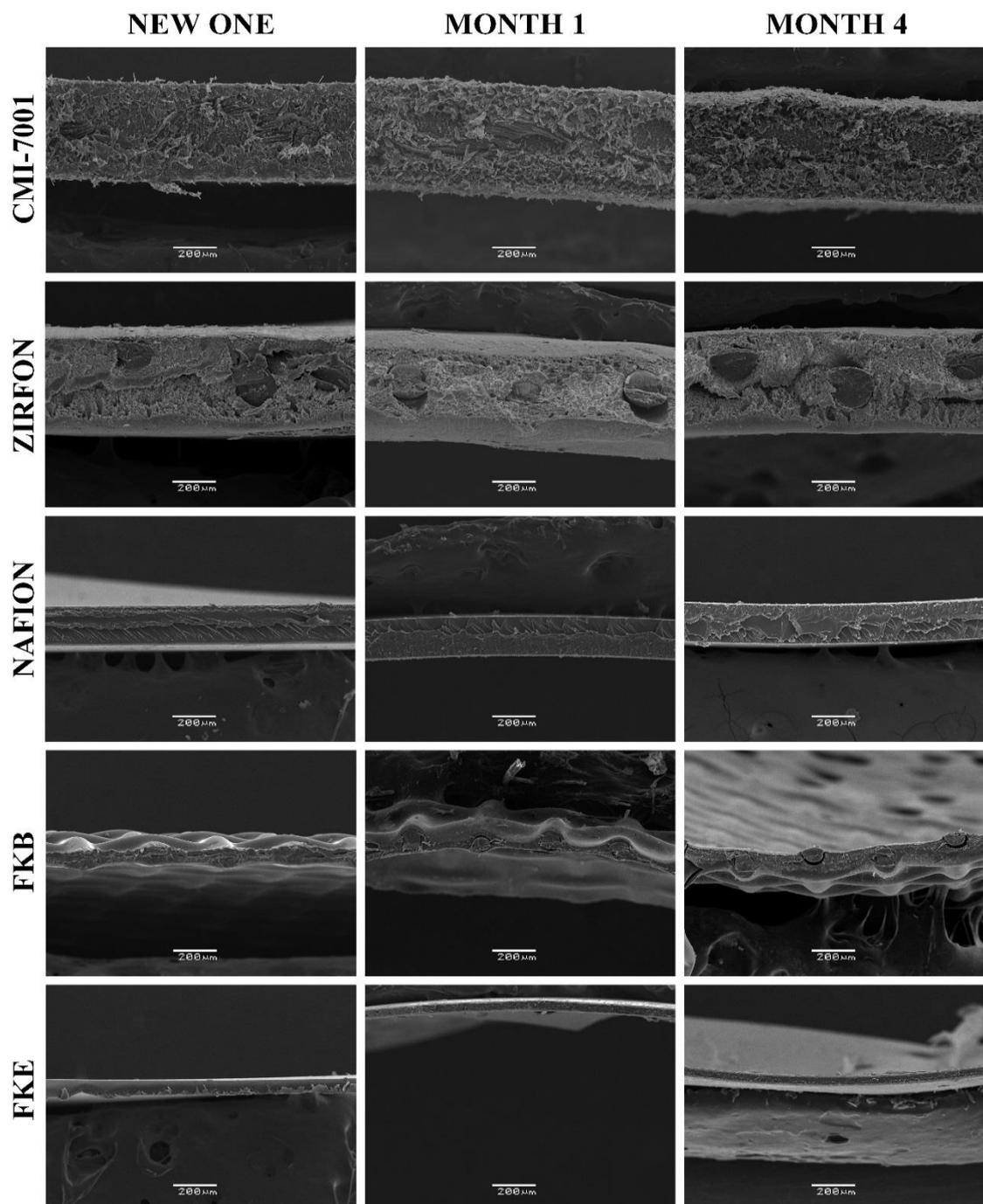
Figure 2. Cross-sectional SEM images of new membranes after 1 and 4 months of operation (90x magnification).

Figure 3 also shows a clear divergence in the evolution of Sq on both sides of the membrane; while the anode side displayed a faster increase and a higher surface roughness, the evolution of Sq on the cathode side was more moderate. This difference can be explained by the higher salt concentration and the presence of biomass on the anode side which could be promoting the fouling process.

Thus, on account of these results, when dealing with substrates with a high salts content (e.g.: landfill leachate or seawater) or substrates with planktonic biomass or complex organic compounds (eg.: wastewater, effluent from anaerobic digestion), Zirfon, FKE and FKB membranes may be more advantageous that the CMI and the Nafion.
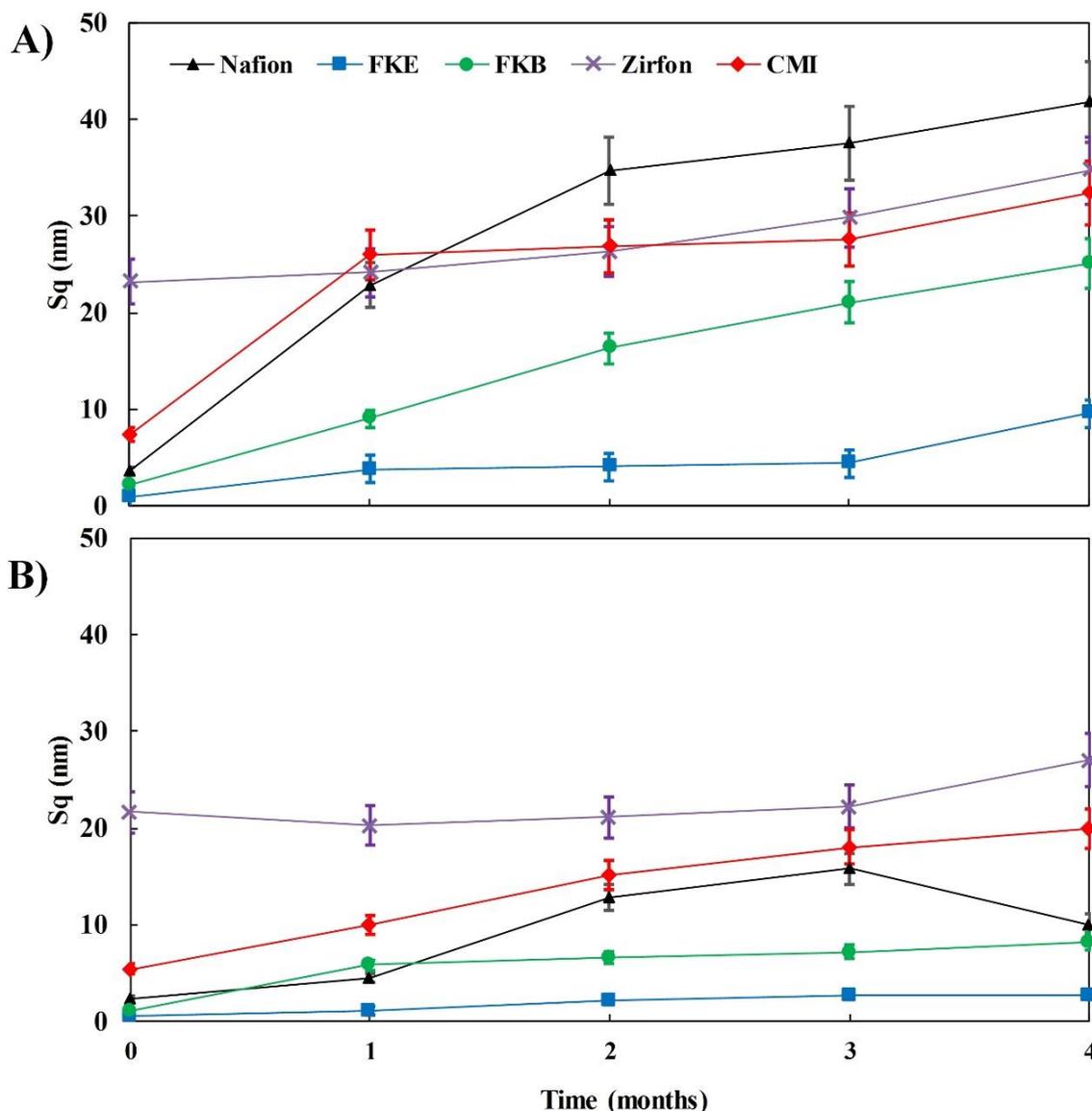
Figure 3. Sq (nm) variation as a function of time on the side in contact with the anolyte (A) and on the side in contact with the catholyte (B).

3.2. Assessment of membrane structural deterioration through TGA

As mentioned before, the lack of any visible deterioration in the membrane structure, as observed in the SEM images (Figure 2), does not necessarily means that the structural stability of the membrane remains unaffected. Indeed, the ageing process can also be affecting the polymer matrix and the functional groups of the membranes. Modifications in any of them were evaluated by monitoring the changes in thermal stability of the samples (Figure 4).

The CMI-7000 consists of cross linked gel polystyrene with divinylbenzene and sulphonic acid as the functional groups [23]. The peak that appears on the TGA profiles between 400 °C and 490 °C (Figure 4A) is attributed to the decomposition of the polystyrene chains together with $-SO_3H^-$ groups, while the peak above 500 °C would most likely be ascribed to the decomposition of the residual solvent from the manufacturing process that is not anchored to the matrix and lost with use. The TGA profiles show a clear divergence between the new and the used membranes: the two peaks that appear on the unused membrane merge into just one peak in used membranes and get displaced towards low temperatures. Beyond this change, there is no evidence of degradation along time, that is, the membrane structure remains fairly stable after this first month of operation.
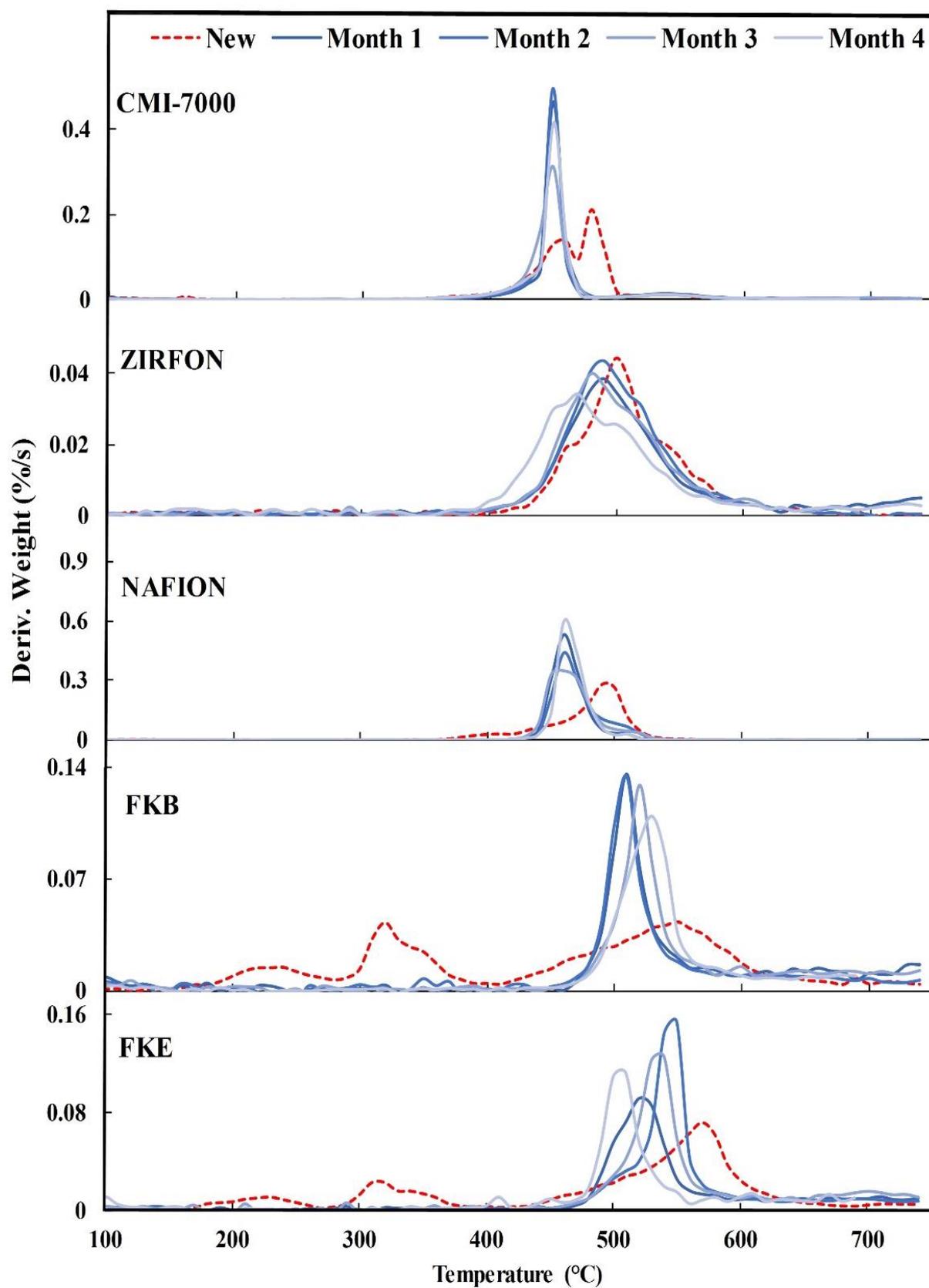
Figure 4. Thermogravimetric analysis of the membranes before (red dash line) and after 1, 2, 3 and 4 months of operation (gradient of blue lines).

For the Zirfon membrane, which consists of a hydrophilic polyphenylene sulphide fabric coated with a mixture of a polymer and zirconium oxide [24], the degradation patter was more gradual and continued after the first month. However, in this case it is difficult to establish a relation between the peaks that appear in the TGA profile and the degradation of any of the compounds that integrate the membrane because there is scant information about the characteristic of the Zirfon membrane in the technical and scientific literature.

The Nafion membrane is a perfluorinated membrane fabricated of carbon–fluorine backbone chains, with perfluoro side chains, containing sulfonic acid groups as the functional groups [24]. For the fresh membrane, the thermal degradation reaches its maximum rate at 500 °C (attributed to the sum of a series–parallel degradation reactions of both the polymer and the functional group [25]) as evidenced by the peak in the TGA profile (Fig. 3C). This peak gets displaced towards lower temperatures (460 °C) after the first month, probably as a result of the loss of the protective layer. The TGA profiles get unaltered in the samples taken in the following months, thus showing a remarkable chemical and thermal stability similarly to that observed in the CMI-7000.

The FKB and FKE are both based on perfluorinated sulfonic acid and are manufactured by the same company (Fumatech) [26]. For both, the fresh membranes present two transitions of mass loss at around 230 and 320 °C, which are attributed to stabilizing agents and another wider one, between 400 and 600 °C, which is attributed to the degradation of sufonated polyether ketones. After the first month of use, the first peak at 320 °C almost disappears in both membranes (because of the removal of the stabilizing agents) and the second peak (at 550 °C) moves to lower temperatures, showing a degradation pattern similar to that of the Zirfon.

Overall, these results show that Nafion and CMI-7000 have an excellent thermal stability in long-term operation, in contrast to Zirfon, FKB and FKE that follow a moderate degradation pattern along time.

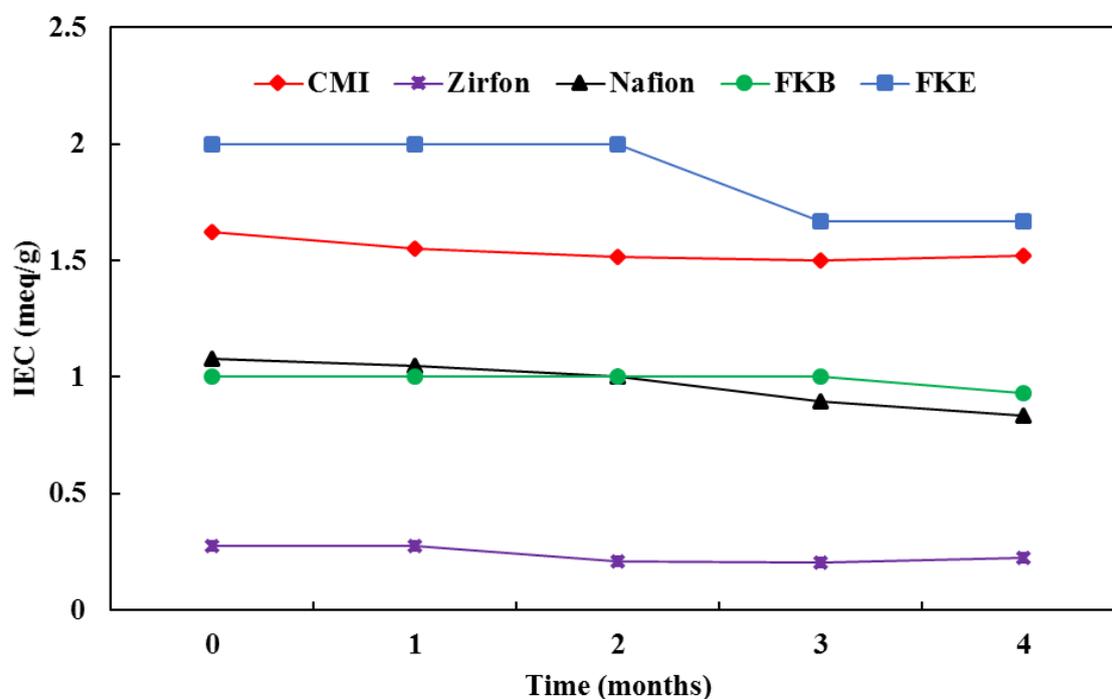*3.3. Assessment of electrochemical properties through IEC*

Figure 5. Evolution of Ion Exchange Capacity (meq/g) along operation time.

The ion exchange capacity (IEC) is the number of fixed charges inside the cation exchange membrane per unit of weight of the dry polymer. The importance of this parameter lays in the fact that IEC is indirectly linked to the proton conductivity of the polymer [27,28] and thus it affects other

important membrane properties such as its electrical resistance [29]. Figure 5 illustrates the evolution of the IEC values along the four months of operation. It shows that IEC did not changed substantially for any of them, except for the FKE, where a clear drop appears between the third and the fourth month of operation with a descent of 18% (although it still kept the highest IEC value). The Nafion membrane underwent a similar reduction (20%), but in this case it was a more gradual one.

3.4. MEC performance and final comments

Cation exchange membranes play a key role on both the economic feasibility and on the electrochemical performance of BES. Assessing their long-term stability becomes, thus, a key issue in process design and cost calculation [30]. Overall, our results show that, at least from the ageing perspective, there is not an ideal cation exchange membrane (among those commercially available) for BES. For instance, the chemical structure of membranes such as FKE, that are less prone to fouling and biofouling (on account of their resilience to surface deterioration) and that score the highest IEC, seem to degrade more rapidly as revealed by the thermal analysis. In contrast, CMI-7000 and even Nafion, which display a remarkable thermal stability after the first month of operation (initial degradation can be attributed to the loss of the protective layer) show a rapid increase of surface roughness and therefore of fouling.
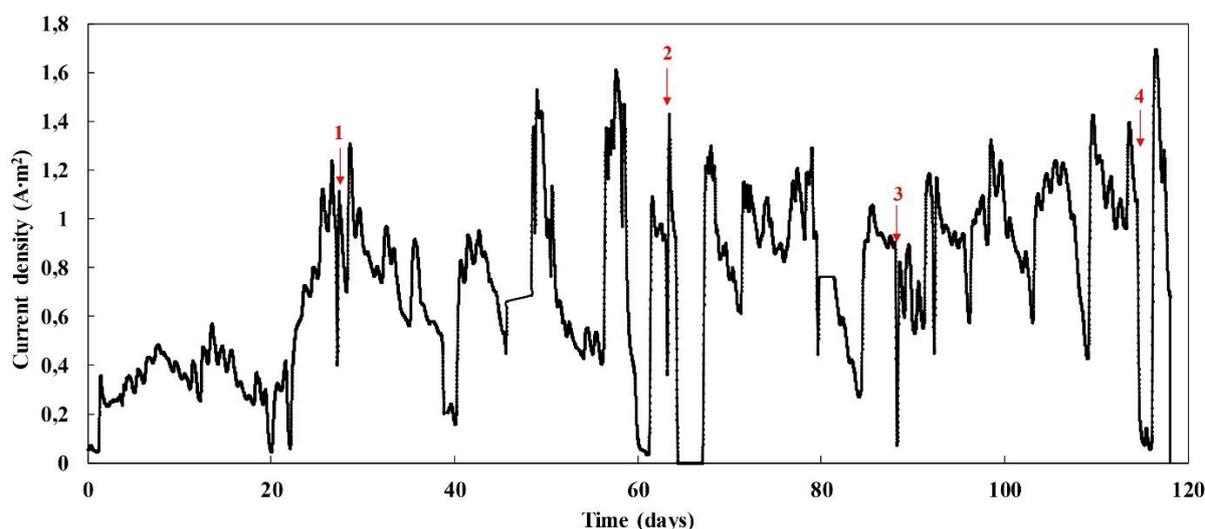

Figure 6. Current density profile over the 120 days periods of operation (Arrows indicate membrane sampling at 1, 2, 3 and 4 months).

Here, it is important to bring to mind that the membranes investigated in this study are typically used in conventional electrochemical systems where current densities can be as high as 10,000 $A \cdot m^{-2}$ [31]. This contrasts with the ~1 $A \cdot m^{-2}$ (Figure 6) measured in our cell, which is an usual current density for BES [32] but highlights the low electrical stress to which conventional membranes are subjected in BES applications. In other words, existing commercial membranes are somehow "oversized" when used in BES. This, of course, would not be problem if it were not for the relatively large cost that these membranes have (Table 1). The challenge is thus to develop "tailor-made" membranes, that can show a fair long-term stability and resilience, with an economic cost that does no threat the commercial development of BES. In this regard, new developments that can provide similar or even better results than commercial membranes at a cheaper cost are already underway [22]. These advances are also helping to expand the range of applications of BES [33,34], opening new exciting possibilities and paving their way towards practical applicability.

4. Conclusions

The ion exchange membrane explains much of the cost of BES and its durability has a marked impact on their economic feasibility. In this study, we compared the ageing process of 5 commercially available cation exchange membranes. Nafion and CMI-7000 showed a remarkably robust chemical structure, although they suffer the greatest surface modification. This revealed a tendency to promote fouling and biofouling that was more pronounced than in FKB and, specially, than in FKE. The ion exchange capacity, which is related to the electric conductivity of the membranes, showed a moderate decay in all membranes. Despite these apparent signs of deterioration, the current density kept almost constant (~1 A m^{-2}) which suggest that the studied membranes can maintain their electrochemical performance within the demanding environment of BES.

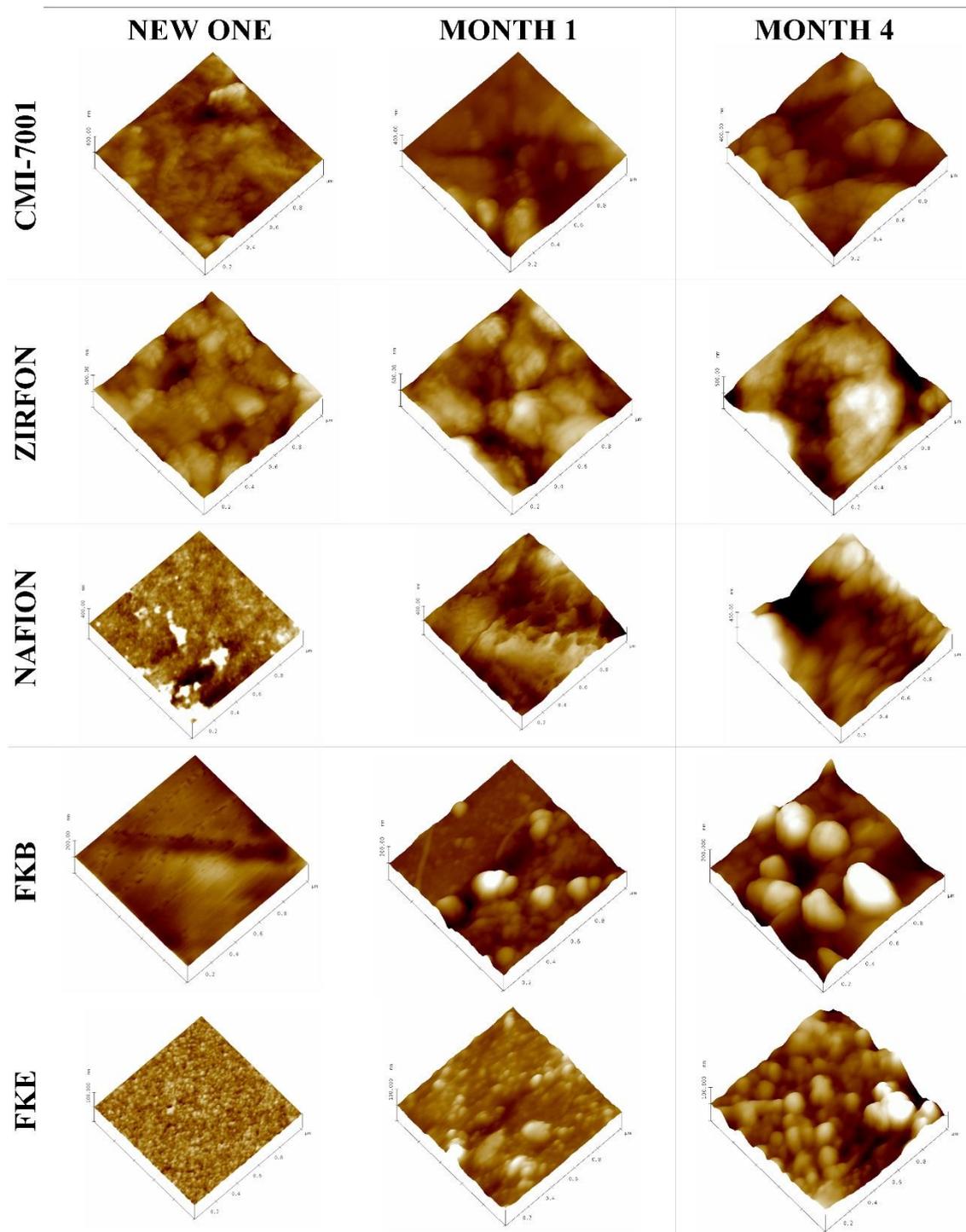**Appendix A- Atomic Force Microscopy images**

Figure A1. Membrane surface images obtained by AFM for the new membrane and after 1 and 4 months of operation.

References

1. Zhang, S.; Bao, R.; Lu, J.; Sang, W. Simultaneous sulfide removal, nitrification, denitrification and electricity generation in three-chamber microbial fuel cells. *Sep. Purif. Technol.* **2018**, *195*, 314–321.

2. Li, S.; Chen, G.; Anandhi, A. Applications of Emerging Bioelectrochemical Technologies in Agricultural Systems: A Current Review. *Energies* **2018**, *11*.

3. San-Martín, M.I. Bioelectrochemical Systems for Energy Valorization of Waste Streams. In; Leicester, D.D., Ed.; IntechOpen: Rijeka, 2018; p. Ch. 8 ISBN 978-1-78923-711-5.

4. Escapa, A.; Mateos, R.; Martínez, E.J.; Blanes, J. Microbial electrolysis cells: An emerging technology for wastewater treatment and energy recovery. From laboratory to pilot plant and beyond. *Renew. Sustain. Energy Rev.* **2016**, *55*, 942–956.

5. Sleutels, T.H.J.A.; ter Heijne, A.; Kuntke, P.; Buisman, C.J.N.; Hamelers, H.V.M. Membrane Selectivity Determines Energetic Losses for Ion Transport in Bioelectrochemical Systems. *ChemistrySelect 2*, 3462–3470.

6. Leong, J.X.; Daud, W.R.W.; Ghasemi, M.; Liew, K. Ben; Ismail, M. Ion exchange membranes as separators in microbial fuel cells for bioenergy conversion: A comprehensive review. *Renew. Sustain. Energy Rev.* **2013**, *28*, 575–587.

7. Cecconet, D.; Callegari, A.; Capodaglio, G.A. Bioelectrochemical Systems for Removal of Selected Metals and Perchlorate from Groundwater: A Review. *Energies* 2018, *11*.

8. Tartakovsky, B.; Kleiner, Y.; Manuel, M. Bioelectrochemical anaerobic sewage treatment technology for Arctic communities. *Environ. Sci. Pollut. Res.* **2017**, 0–6.

9. Yan, T.; Ye, Y.; Ma, H.; Zhang, Y.; Guo, W.; Du, B.; Wei, Q.; Wei, D.; Ngo, H.H. A critical review on membrane hybrid system for nutrient recovery from wastewater. *Chem. Eng. J.* **2018**, *348*, 143–156.

10. San-Martin, M.I.; Leicester, D.D.; Heidrich, E.S.; Alonso, R.M.; Mateos, R.; Escapa, A. Bioelectrochemical Systems for Energy Valorization of Waste Streams. In *Energy Systems and Environment*; IntechOpen, 2018.

11. Hernández-Fernández, F.J.; de los Ríos, A.P.; Mateo-Ramírez, F.; Juarez, M.D.; Lozano-Blanco, L.J.; Godínez, C. New application of polymer inclusion membrane based on ionic liquids as proton exchange membrane in microbial fuel cell. *Sep. Purif. Technol.* **2016**, *160*, 51–58.

12. Sevda, S.; Dominguez-Benetton, X.; Vanbroekhoven, K.; Sreekrishnan, T.R.; Pant, D. Characterization and comparison of the performance of two different separator types in air–cathode microbial fuel cell treating synthetic wastewater. *Chem. Eng. J.* **2013**, *228*, 1–11.

13. Li, W.-W.; Sheng, G.-P.; Liu, X.-W.; Yu, H.-Q. Recent advances in the separators for microbial fuel cells. *Spec. Issue Biofuels - II Algal Biofuels Microb. Fuel Cells* **2011**, *102*, 244–252.

14. Dammak, L.; Larchet, C.; Grande, D. Ageing of ion-exchange membranes in oxidant solutions. *Sep. Purif. Technol.* **2009**, *69*, 43–47.

15. Collette, F.M.; Lorentz, C.; Gebel, G.; Thominette, F. Hygrothermal aging of Nafion®. *J. Memb. Sci.* **2009**, *330*, 21–29.

16. Mateos, R.; Alonso, R.; Escapa, A.; Morán, A. Methodology for Fast and Facile Characterisation of Carbon-Based Electrodes Focused on Bioelectrochemical Systems Development and Scale Up. *Materials (Basel).* **2017**, *10*, 79.

17. del Pilar Anzola Rojas, M.; Mateos, R.; Sotres, A.; Zaiat, M.; Gonzalez, E.R.; Escapa, A.; De Wever, H.; Pant, D. Microbial electrosynthesis (MES) from CO2 is resilient to fluctuations in renewable energy supply. *Energy Convers. Manag.* **2018**, *177*, 272–279.

18. Silva, V.; Montalvillo, M.; Carmona, F.J.; Palacio, L.; Hernández, A.; Prádanos, P. Prediction of single salt

rejection in nanofiltration membranes by independent measurements. *Desalination* **2016**, *382*, 1–12.

19.   Johnson, D.; Hilal, N. Characterisation and quantification of membrane surface properties using atomic force microscopy: A comprehensive review. *Desalination* 2015, *356*, 149–164.

20.   Xu, J.; Sheng, G.-P.; Luo, H.-W.; Li, W.-W.; Wang, L.-F.; Yu, H.-Q. Fouling of proton exchange membrane (PEM) deteriorates the performance of microbial fuel cell. *Water Res.* **2012**, *46*, 1817–1824.

21.   Meng, F.; Liao, B.; Liang, S.; Yang, F.; Zhang, H.; Song, L. Morphological visualization, componential characterization and microbiological identification of membrane fouling in membrane bioreactors (MBRs). *J. Memb. Sci.* **2010**, *361*, 1–14.

22.   Zinadini, S.; Zinatizadeh, A.A.; Rahimi, M.; Vatanpour, V.; Rahimi, Z. High power generation and COD removal in a microbial fuel cell operated by a novel sulfonated PES/PES blend proton exchange membrane. *Energy* **2017**, *125*, 427–438.

23.   CMI-7000 Cation Exchange Membranes : Membranes International Inc.

24.   ZIRFON PERL UTP 500 - Specialty Products.

25.   Deng, Q.; Wilkie, C.A.; Moore, R.B.; Mauritz, K.A. TGA–FTi.r. investigation of the thermal degradation of Nafion® and Nafion®/[silicon oxide]-based nanocomposites. *Polymer (Guildf).* **1998**, *39*, 5961–5972.

26.   Products - fumatech GmbH.

27.   Navessin, T.; Holdcroft, S.; Wang, Q.; Song, D.; Liu, Z.; Eikerling, M.; Horsfall, J.; Lovell, K. V. The role of membrane ion exchange capacity on membrane|gas diffusion electrode interfaces: a half-fuel cell electrochemical study. *J. Electroanal. Chem.* **2004**, *567*, 111–122.

28.   Chuy, C.; Basura, V.I.; Simon, E.; Holdcroft, S.; Horsfall, J.; Lovell, K. V Electrochemical Characterization of Ethylenetetrafluoroethylene-g-polystyrenesulfonic Acid Solid Polymer Electrolytes. *J. Electrochem. Soc.* **2000**, *147*, 4453–4458.

29.   Wilhelm, F.G.; Pünt, I.G.M.; van der Vegt, N.F.A.; Strathmann, H.; Wessling, M. Cation permeable membranes from blends of sulfonated poly(ether ether ketone) and poly(ether sulfone). *J. Memb. Sci.* **2002**, *199*, 167–176.

30.   Giorno, L.; Drioli, E.; Strathmann, H. Ion-Exchange Membrane Characterization BT   - Encyclopedia of Membranes. In; Drioli, E., Giorno, L., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2016; pp. 1052–1056 ISBN 978-3-662-44324-8.

31.   Peighambardoust, S.J.; Rowshanzamir, S.; Amjadi, M. Review of the proton exchange membranes for fuel cell applications. *Int. J. Hydrogen Energy* **2010**, *35*, 9349–9384.

32.   Rahimnejad, M.; Adhami, A.; Darvari, S.; Zirepour, A.; Oh, S.-E. Microbial fuel cell as new technology for bioelectricity generation: A review. *Alexandria Eng. J.* **2015**, *54*, 745–756.

33.   Kuntke, P.; Zamora, P.; Saakes, M.; Buisman, C.J.N.; Hamelers, H.V.M. Gas-permeable hydrophobic tubular membranes for ammonia recovery in bio-electrochemical systems. *Environ. Sci. Water Res. Technol.* **2016**, *2*, 261–265.

34.   Yuan, H.; He, Z. Integrating membrane filtration into bioelectrochemical systems as next generation energy-efficient wastewater treatment technologies for water reclamation: A review. *Bioresour. Technol.* **2015**, *195*, 202–209.