Koók, L., **Rosa, L.F.M.**, **Harnisch, F.**, Žitka, J., Otmar, M., Nemestóthy, N., Bakonyi, P., Kretzschmar, J. (2022):
Functional stability of novel homogeneous and heterogeneous cation exchange membranes for abiotic and microbial electrochemical technologies
J. Membr. Sci. **658** , art. 120705

http://dx.doi.org/10.1016/j.memsci.2022.120705

Functional stability of novel homogeneous and heterogeneous cation exchange membranes for abiotic and microbial electrochemical technologies

László Koók[1], Luis F. M. Rosa[2], Falk Harnisch[2], Jan Žitka[3], Miroslav Otmar[3], Nándor Nemestóthy[1], Péter Bakonyi[1], Jörg Kretzschmar[4,*]

[1]Research Group on Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem ut 10, 8200 Veszprém, Hungary

[2]Helmholtz-Centre for Environmental Research GmbH – UFZ, Department Environmental Microbiology, Permoserstrasse 15, Leipzig 04318, Germany

[3]Institute of Macromolecular Chemistry, AS CR, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

[4]DBFZ Deutsches Biomasseforschungszentrum gemeinnützige GmbH, Biochemical Conversion Department, Torgauer Strasse 116, Leipzig 04347, Germany

* Corresponding Author: Dr. Jörg Kretzschmar

Tel: +49 (0)341 2434-419

Email: joerg.kretzschmar@dbfz.de

Abstract

Two novel cation exchange membranes (CEM) denoted as PSEBS SU and CF22R14 were examined for two electrochemical applications and compared to a commercial membrane (Fumasep FKE). Application in microbial electrolysis cells (MEC) and an abiotic electrochemical cells (EC) were selected as low and high current density systems (~1 A m^{-2} and 50 A m^{-2}, respectively). Hydration number (λ), ion exchange capacity (IEC) and ionic conductivity (σ), as well as their alteration after 10 days were studied. λ was stable after MEC operation, however EC mode caused remarkable changes and a decrease of λ (by -8.2 ± 0.3, -13.8 ± 0.8 and -39.3 ± 8.8% for FKE, PSEBS SU and CF22R14, respectively). The decrease of IEC was significant for each membrane regardless of the operation mode. However, only MEC operation led to reversible functionality losses, whereas EC mode caused permanent decrease of IEC (87.9 ± 2.8, 85.3 ± 3.8 and 46.6 ± 4.4% re-activation efficiency for FKE, PSEBS SU and CF22R14, respectively). The EC operation resulted in more severe loss of σ for each CEM, among which PSEBS SU showed the best re-activation efficiency (74.9 ± 8.1%). In general, the membrane properties were much more impaired during EC operation due to higher current densities.

Keywords: Cation exchange membrane; functional stability; microbial electrolysis cell; ion exchange capacity; ionic conductivity

1. Introduction

Ion exchange membranes (IEM) are functionalized and charged polymer-based thin materials, which facilitate the selective transport of ionic compounds [1]. IEMs are used for a variety of electrochemical processes, such as electrodialysis (ED) [2], reverse electrodialysis (RED) [3], electrodeionization [4], diffusion- and Donnan-dialysis [5], fuel cell technology [6,7], etc. Fields of application for IEM also include microbial electrochemical technologies (MET). MET are technology platforms based on merging microbial and electrochemical conversions for electricity generation, desalination, waste treatment or production of value-added chemicals [8–10]. However, the reactors used for MET that are denominated as bioelectrochemical systems (BES) differ in many cases significantly from abiotic electrochemical systems concerning, e.g., electrolyte composition and concentration, electrode potential, current density, operational modes, flow and reaction rates [11]. Thus, most of the commercially available IEM are not specifically designed for BES [12].

In BES, the most frequently used IEM are cation exchange membranes (CEMs), among which Nafion-based proton exchange membranes (PEM) represent a standard reference material [13,14]. It was shown previously, when using Nafion-based IEM in BES the charge balancing ion transfer is dominated by cations as well as anions other than H^+ and OH^- [15–18]. Therefore, the development of alternative IEM being flexible and possessing excellent functional stability are desired. Such materials must sufficiently overcome negative effects of biofouling, chemical scaling, fluctuations of solution pH, and in case of some applications concentration polarization at the polarized membrane surface [19–23]. These stress factors may lead to reversible or irreversible loss of functionality through passivation or even loss of functional groups (e.g. hydrophilic RSO_3^- sulfonic acid groups in case of CEM) [24–26].

The functional stability of IEM can be characterized by determining and evaluating key membrane properties and their alterations over time and in different application environments. Hydrophobic and hydrophilic properties of membranes are represented by their contact angle and water uptake behavior (hydration number, λ) [27]. Although adequate IEM functionality requires sufficient hydration, too much swelling can cause structural deterioration of the polymers [28]. Furthermore, the decrease in membrane hydration number during operation is an implicit indicator of loss of available hydrophilic functional groups. As a direct measure of the number of functional groups relative to the dry polymer weight, ion exchange capacity (IEC) is determined, usually via titration methods [27]. Strongly linked to the aforementioned properties, ionic conductivity (σ) of IEM is a frequently used parameter for quantifying the electric field-driven ion transport [29].

Various attempts are described in literature to tailor novel IEM for BES, fulfilling the aforementioned requirements while trying to ensure economic viability [13,30,31]. In this work, two novel CEM (denoted as PSEBS SU and CF22R14) were tested in abiotic electrochemical systems and BES. It was shown in our previous works that PSEBS SU possesses promising features for BES, such as sufficient σ at low electrolyte concentrations [32,33]. The CF22R14 was successfully employed for microbial electrochemical hydrogen production [33]. The aim of the present study was to investigate how functional properties of these alternative membrane materials change when used for short-term (i.e. weeks) in different applications (i.e. at high current density in abiotic electrochemical systems, and at low current density in BES). IEC, λ and σ alterations of pristine, used and chemically re-activated CEM was evaluated as main features linked to functional stability of the membranes. In addition, the relationship between conductivity and electrolyte properties commonly used for

BES (low acetate concentration, low phosphate buffer strength and initially neutral pH) was studied. The data obtained for the novel membrane materials were compared with a commercial reference CEM.

2. Materials and Methods

2.1. Chemicals

All chemicals used in this work were at least of analytical grade. CH_3COONa (≥ 99.0 %), Na_2HPO_4 (≥ 99.0 %), NaH_2PO_4 (≥ 98.0 %), NaCl (≥ 99.0 %), HCl (36 % solution) and NaOH (≥ 98 %) were purchased from Merck (Darmstadt, Germany). N_2 purging gas (99.995 %, V/V) was obtained from Messer Hungarogáz Kft (Budapest, Hungary). All solutions were prepared with distilled water.

2.2. Ion exchange membranes and conditioning procedure

In this work, three different CEM were applied and tested. 1) FKE (FuMa-Tech, Bietigheim-Bissingen, Germany), which is a non-reinforced, homogeneous polymer membrane with a thickness of 66 ± 3 μm (swollen state). 2) CF22R14, a heterogeneous, developmental RALEX® membrane (MEGA/MemBrain, Czech Republic) [33] with 222 ± 13 μm average thickness. CF22R14 is made of a strong acidic ion exchanger and polyolefin binder matrix. 3) PSEBS SU, is a polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-based homogeneous CEM developed at the Institute of Macromolecular Chemistry, Czech Academy of Sciences [34]. Its thickness in swollen state is 158 ± 12 μm.

The pre-conditioning, as well as the re-activation of the CEM were carried out by consecutive immersion into distilled water, 1 M HCl and 1 M NaOH solution [35,36].

Firstly, the dry CEM samples in Na^+ form were put in H_2O, then in HCl (H^+ form), H_2O, NaOH (Na^+ form), H_2O, and finally, in HCl resulting in H^+ form. Each conditioning step took 30 min at 25 °C, and after activation, the membranes were stored in distilled water until use [35].

2.3. MEC and EC operation

3D printed rectangular 4-chamber test cells (**Fig. 1**) printed with polylactic acid (BASF Ultrafuse, 1.75 mm, BASF Forward AM, Heidelberg, Germany) were used as microbial electrolysis cells (MEC) and abiotic electrochemical cells (EC), as well as for membrane polarization experiments (see section 2.5). The reactor design enabled flexible chamber division by using the three possible insertion slots of the membrane panels (Appendix, **Fig. A.1**).

Triplicate MECs were assembled as follows: each rectangular 4 chamber test cell was divided in 4 compartments, where both halves of the cells consisted of a cathode chamber and an anode chamber separated by the membrane under investigation, while in the central slot, a plastic sheet (HDPE, A-Plast, Hungary) was used as an impermeable barrier, creating two MEC per rectangular 4-chamber test cell. This way, 2 MEC could operate independently in one 4-chamber test cell. The anolyte (with a total working volume of 115 mL) comprised of 50 mM phosphate buffer solution (PBS) inoculated with 10 % (v/v) anaerobic sludge, 5 mM sodium acetate, 1-1 mL modified Wolin's mineral solution (excluding $Na_2SeO_3 \times 5\ H_2O$ and $Na_2WO_4 \times 2\ H_2O$) and vitamin solution (according to DSMZ 141), as well as 100 μL selenite-tungstate solution (according to DSMZ 385). The anaerobic sludge was the effluent of a biogas fermenter fed with municipal wastewater, collected at Bakonykarszt Zrt, Veszprém, Hungary. The catholyte was 50 mM PBS with a total working volume of 45 mL. 1 cm × 1 cm Pt electrodes (Pt foil, purity 99,95%, thickness = 0.12 mm, HMW Hauner GmbH & Co. KG Röttenbach, Germany) were applied as cathodes, while 2 cm long graphite rods with 0.5 cm diameter (99.995 % purity, Merck, Darmstadt, Germany) served as anodes. The growth of anodic biofilms was performed according to [37]. During MEC operation, an Ag/AgCl (3 M KCl, +0.207 mV vs. SHE) reference electrode (OP-0820P, Radelkis, Budapest, Hungary) was placed in the anolyte, and the anode potential was set to 0.2 V using a potentiostat (PalmSens 3, Houten, Netherlands). The membranes were tested for five cycles. The length of one cycle was determined by substrate depletion and hence, current decrease. After substrate depletion the solution was replaced by fresh anolyte.

The EC operation was carried out by using multistep chronopotentiometry (PalmSens 3, Houten, Netherlands), using the same buffer compositions as for MEC operation. The applied current density (i, related to the membrane surface area, A_M) profile was programmed to mimic the MEC cycles as follows: the current density curves had a sum length of 48 h, starting from zero to 10 A m^{-2} in the first 7 h, then increased to 25 A m^{-2} for 8 h, followed by a 18 h long peaking period at 50 A m^{-2}. The current density was then gradually decreased back to 25 A m^{-2}, 10 A m^{-2} and finally, zero. Thus, five consecutive cycles were run (similarly to MEC operation in terms of cycle duration) in 240 h.

2.4. Membrane properties

Acid-base titration method was used to determine IEC of the membranes in different states (pristine, used, re-activated) [38,39] as detailed recently [33]. Briefly, IEC is based on measuring the OH^- concentration decrease of an alkaline solution over the contact time with a CEM sample previously brought to H^+-form.

λ was determined based on the water content (φ) and IEC of the membranes [39]. φ was determined by comparing the dry and swollen sample weights, measured in a Sartorius R200D analytical balance with 0.01 mg resolution (Sartorius, Göttingen, Germany). Thereafter, λ was calculated according to Eq. 1, considering IEC, φ and the molar mass of water (M_W).

$$\lambda = \frac{\varphi}{IEC\, M_W\, 100} \tag{1}$$

In order to determine dry membrane mass, the samples were vacuum-dried for at least 1 h at 25 °C. The swollen membrane mass was determined after keeping the dry samples in distilled water overnight, and the excess water was gently blotted from the membrane surface with tissue paper.

The alterations in the structural properties of the various membranes after use were characterized by optical microscopy, using a light microscope at 400x total magnification (Primostar, Carl Zeiss, Jena, Germany). The optical images of the samples were recorded using a MikrOkular Full HD eyepiece camera (Bresser, Rhede, Germany). The thickness of the membranes (δ_M) (in swollen state) was determined by an analogue thickness gauge (Käfer F 1000/30, Villingen-Schwenningen, Germany) with 1 μm accuracy.

2.5. Membrane polarization and ionic conductivity

The σ of a membrane is considered as one of the main features for evaluating membrane stability. Accordingly, polarization measurements were conducted in a set of experimental setups using pristine, used, and re-activated membranes. A design of experiment (DoE) approach was created with acetate concentration (c_{Ac} = 5, 10 and 20 mM), phosphate buffer concentration (c_{PBS} = 25, 50 and 100 mM) and electrolyte pH (pH = 6, 7 and 8) as factors, and membrane conductivity as dependent variable. The experimental settings were determined as follows (**Table 1**).

Table 1 – Factor value combinations for the membrane polarization measurements

pH (-)	c_{Ac} (mM)	c_{PBS} (mM)
6	5	25
6	5	100
6	10	50
6	20	25
6	20	100
7	5	50
7	10	25
7[*]	**10**[*]	**50**[*]
7	10	100
7	20	50
8	5	25
8	5	100
8	10	50
8	20	25
8	20	100

[*] Central point carried out in triplicate

The measurements were conducted using the same reactor configuration as in MEC and EC experiments, however, the electrode and membrane arrangement was modified as follows (**Fig. 1**).

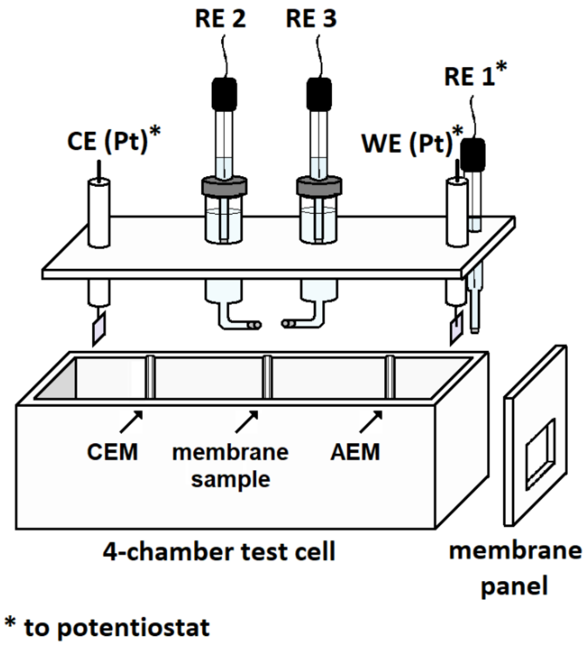

Fig. 1 – Scheme of the membrane polarization cell setup, WE: working electrode, CE: counter electrode, RE: reference electrode, CEM: cation exchange membrane, AEM: anion exchange membrane, Pt: platinum.

The membrane under investigation was placed in a membrane panel in the middle of the cell. 1 × 1 cm Pt sheet electrodes (WE and CE) were placed in the two sides of the cell. An Ag/AgCl (3 M KCl) reference electrode (OP-0820P, Radelkis, Budapest, Hungary) (RE1) was placed next to WE, while two other Ag/AgCl reference electrodes (RE2 and RE3, identical to R1) were positioned at the two sides of the tested membrane. RE2 and RE3 were equipped with Luggin capillaries being here glass capillaries with a porous glass frit at their tip and filled with 3 M KCl solution [40]. An anion exchange membrane (AEM, PSEBS DABCO, commercialized by TailorMem company under the trade mark Hollex ADL 911 NR [41]) was used in a membrane panel to separate the membrane under investigation and WE, while the CE and the membrane under investigation were separated by a CEM (Fumasep FKE). The four compartments of the cell were filled with the same electrolyte (according to **Table 1**), and were stirred at 150 rpm. WE, CE and RE1 were connected to a potentiostat/galvanostat (Palmsens3, Palmsens, Houten, Netherlands) in order to perform chronopotentiometric polarization with applied current densities between 0.625 – 7.5 A m^{-2} (relative to the projected membrane surface area). Each current density was kept for 5 min, and the occurring membrane potential difference (U) between RE2 and RE3 was monitored by using a battery-driven 5½ digit multimeter (Metrix MTX3281, Chauvin Arnoux, Paris, France). The stationary potential difference was recorded, and based on the related current (I) values, the I-U data pairs were used to determine the resistance of the membrane+electrolyte (R_{M+E}) as a slope of the I-U curves, according to Ohm's law. By performing the procedure without any membrane in the central position the background electrolyte resistance (R_E) was determined. The pure membrane resistance (R_M) is then gained by subtracting R_E from the R_{M+E}. The membrane conductivity was then calculated based on R_M and the ratio of swollen membrane thickness (δ_M) and surface area (A_M) according to Eq. 2 [42].

$$\sigma = \frac{\delta_M}{R_M \cdot A_M} \qquad (2)$$

2.6. Data evaluation and statistics

In order to ensure reliable data evaluation, all – MEC and EC – measurements were done in triplicate. Similarly, membrane characterization was done in three independent replicates. Standard deviations (SD), standard errors (SE) and (95 %) confidence intervals (CI) are presented alongside the mean and median values. After carrying out ANOVA, the significance ($p < 0.05$) of differences between main membrane parameters at various membrane conditions was tested by post-hoc Tukey's Honest Significant Difference (HSD) analysis [43]. In case of the membrane conductivity assessment (carried out by DoE), a linear model was fitted (51 data points per membrane type at each condition), and ANOVA was deployed to identify significant ($p < 0.05$) factors using Statistica 8.0.

3. Results and Discussion

3.1. Current profiles, efficiency and pH alterations in MEC and EC operations

The maximum current density (i_{max}, related to the membrane surface area) generated by the MEC operated with the various CEMs was in the range of ca. 0.8 – 1.6 A m^{-2} regardless of the actual membrane type (**Fig. 2.A-C**). In general, the MEC equipped with the PSEBS SU achieved higher i_{max} of 1.10 ± 0.55 A m^{-2}, followed by the FKE membrane with 1.05 ± 0.33 A m^{-2}, while in case of CF22R14 CEM, i_{max} was only 0.95 ± 0.34 A m^{-2}. In our previous study with acetate-fed MEC and MFC the beneficial mass transfer properties of PSEBS SU resulted in a significantly lower cycle operational time compared to commercially available CEM (Nafion 115 and Fumasep FBM) while ensuring similar Coulombic efficiencies [32,33].

In this work, the average operation times of the individual acetate cycles were slightly shorter in case of PSEBS SU (45.8 ± 5.1 h) compared to the other CEMs (46.8 ± 5.7 h and 49.3 ± 6.4 h for CF22R14 and FKE), although the difference was not statistically significant.

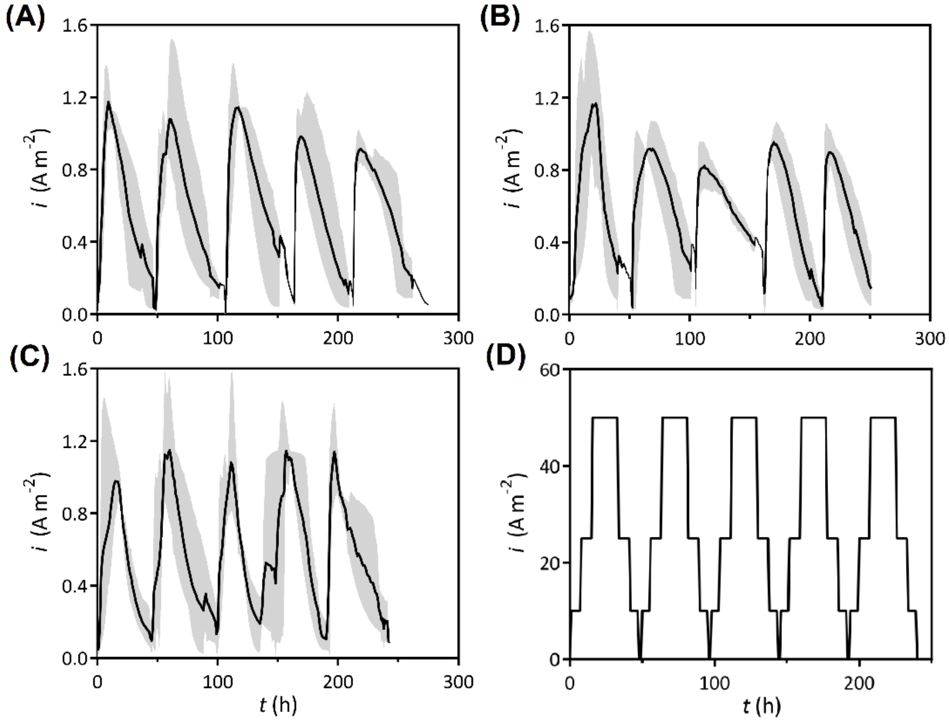

Fig. 2 – Chronoamperometric curves of FKE (A), CF22R14 (B) and PSEBS SU (C) CEMs in MEC mode. D: chronopotentiometric current profile applied in EC operation. Continuous lines show the mean *i* from 3 parallel runs, while the grey area indicates mean *i* ± SD.

Based on the MEC results, the abiotic EC operation was carried out for cycles of 48 h. In the multistep potentiometric experiments, as shown in **Fig 2.D**, *i* was gradually increased up to 50 A m^{-2} (projected to the membrane surface area), representing the range used in electrochemical technologies for resource recovery or wastewater reuse [44,45].

For MEC operation, the pH alterations in the anolyte were relatively low, and somewhat higher in the catholyte during the cycles (**Table 2**).

Table 2 – Anolyte and catholyte pH changes in MEC and EC operation

MEC operation						
Membrane	$pH_{an,in}$	$pH_{cat,in}$	$pH_{an,fin}$	**± 95 % CI**	$pH_{cat,fin}$	**± 95% CI**
FKE	7.2	7.2	6.5	0.35	8.8	0.26
PSEBS SU	7.2	7.2	6.2	0.44	9.1	0.26
CF22R14	7.2	7.2	6.7	0.35	9.2	0.18
EC operation						
Membrane	$pH_{an,in}$	$pH_{cat,in}$	$pH_{an,fin}$	**± 95 % CI**	$pH_{cat,fin}$	**± 95% CI**
FKE	7.2	7.2	4.9	0.44	12.9	0.26
PSEBS SU	7.2	7.2	5.0	0.26	12.8	0.26
CF22R14	7.2	7.2	5.2	0.18	13.0	0.18

There was no significant difference between the extent of anolyte pH change for the various membranes, however, the catholyte pH increase over time of the MEC with CF22R14 was significantly higher ($p = 0.013$) compared to FKE. As expected, the pH change of the electrolytes was more pronounced in the case of EC operation, due to the higher *i* (**Table 2**). The respective decrease of the anolyte and increase of the catholyte pH was similar for each membrane, which is in line with the MEC results. Although there was a significantly higher change in pH of anolyte and catholyte during EC operation compared to MEC mode for each membrane, there was no difference between the obtained pH changes for the different membranes.

3.2. Evaluation of CEM hydration numbers and ion exchange capacity

The swelling properties (such as λ) of ion exchange membrane materials are basic features determining their applicability. Nonetheless, the hydration conditions have to be considered together with other key-factors, e.g. IEC and σ. The hydrophilic functional groups of the membrane (such as RSO_3^- groups) require sufficient hydration to accomplish the selective ion transfer, although a too high water uptake may lead to the undesired distancing of the functional groups, thus, affecting the ion transfer kinetics [46,47].

Consequently, the hydration numbers were determined for CEM in pristine, used and re-activated states, respectively. As it can be seen from **Fig. 3.A-B**, the commercial FKE membrane had the lowest mean λ, followed by PSEBS SU and the CF22R14 for each condition. It was also observed that the swelling was not visible to the naked eye for the two homogeneous membranes, only the heterogeneous CF22R14 membrane showed a slight, but noticeable extension. At the end of the MEC experiments, the used membrane samples showed a minimal, almost negligible decrease of λ, and after chemical re-activation, λ appeared to be similar to that measured for pristine samples (**Fig. 3.A**). The statistical evaluation of the data confirmed that none of the membranes suffered from a significant loss of λ during the ~10 day long MEC operation ($p = 0.8$ to 0.99).

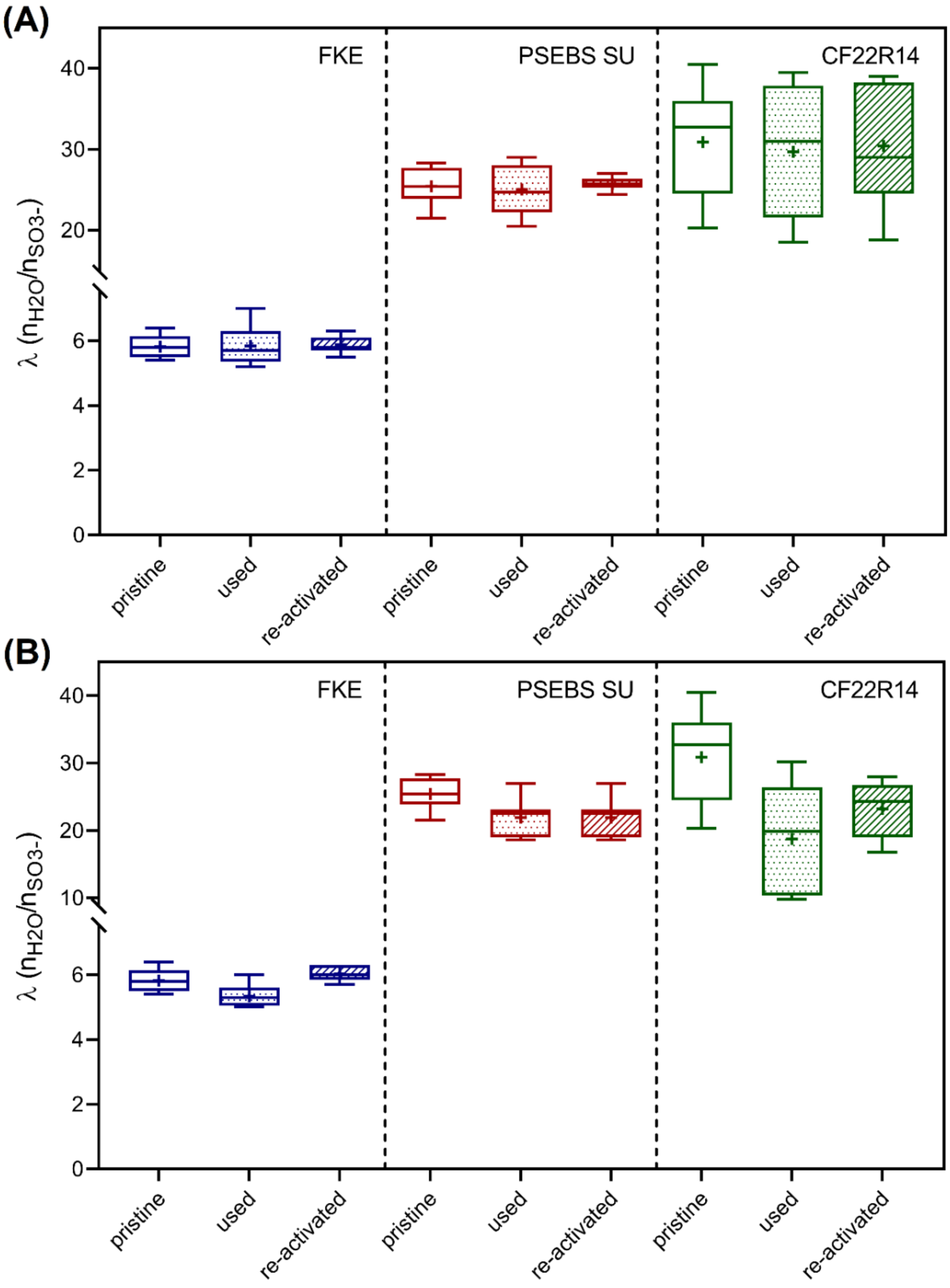

Fig. 3 – Box and Whisker plots of hydration numbers (λ) for CEMs in pristine, used and re-activated state (A: MEC operation; B: EC operation). Boxes indicate 95 % CI, whiskers present minimum and maximum values, while horizontal lines and cross symbols present median and mean, respectively.

λ was determined also after the EC measurements. As it can be seen from **Fig. 3.B**, more significant alterations appeared in λ compared to MEC results most likely as a result of higher *i*. The commercial FKE membrane reflected the most consistent values: after a slight decrease in λ (-8.2 ± 0.3 %, p = 0.0097) for the used sample, λ was sufficiently recovered by chemical re-activation, to match pristine conditions ($p << 0.05$ comparing the used and re-activated states). The PSEBS SU showed a similar trend, although the decrease in λ after use was somewhat higher (-13.8 ± 0.8 %, p = 0.0094). The CF22R14 CEM underwent a significant (p = 0.0021), -39.3 ± 8.8 % decrease, and even after re-activation, only 75 ± 6.7 % of the original λ could be recovered (**Fig. 3.B**). Although the difference between mean λ of the CF22R14 in pristine and re-activated states was not statistically significant (p = 0.054), this membrane showed the less effective λ retainability. As the significance was borderline, clarifying this aspect will require follow-up experiments with longer duration of operation. These results imply that the availability of hydrophilic functional groups became – to some extent – irreversibly hindered in case of CF22R14, while the experimental PSEBS SU membrane was only exposed to reversible impacts, similarly to the FKE membrane.

The functional stability of the membranes can be more explicitly characterized by the IEC values (**Fig. 4.A-B**). IEC is referring to the amount of active functional groups relative to the dry mass of the polymer samples. The pristine homogeneous FKE and PSEBS SU membranes had comparable IECs, of 1.41 ± 0.12 and 1.24 ± 0.08 m*eq* g^{-1}, respectively (**Fig. 4.A**).

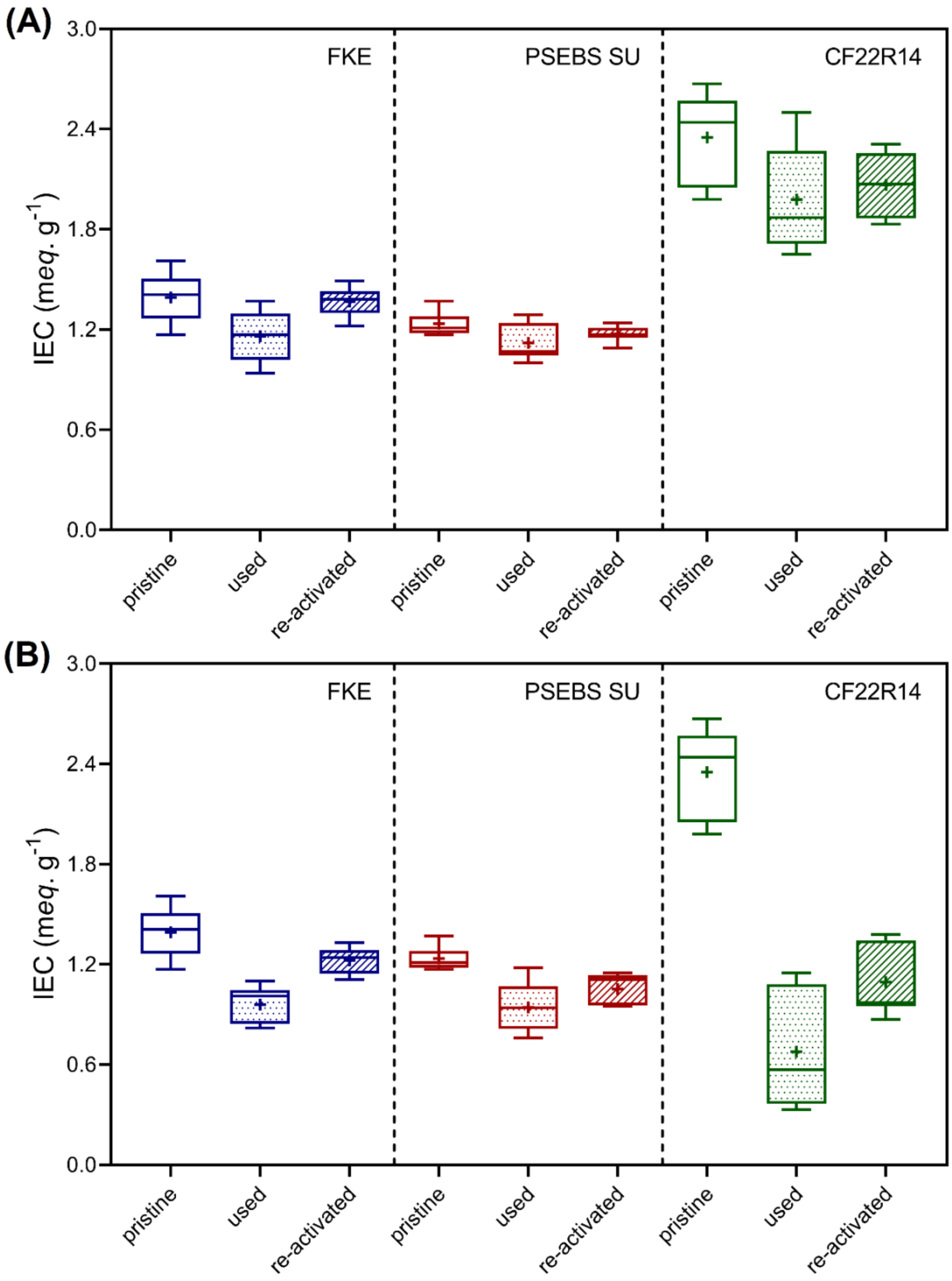

Fig. 4 – Box and Whisker plots of ion exchange capacity (IEC) for CEMs in pristine, used and re-activated state (A: MEC operation; B: EC operation). Boxes indicate 95 % CI, whiskers present minimum and maximum values, while horizontal lines and cross symbols present median and mean, respectively.

Considering other frequently used CEMs, it can be inferred that the studied membranes have sufficient IEC. For example, commonly used Nafion membrane types (such as Nafion 117, 115 or 212) possess IEC from 0.90 to 1.01 m*eq* g^{-1}, while another frequently used material, CMI-7000 CEM has a higher IEC (~1.60 m*eq* g^{-1}) [12]. It is of note that the heterogeneous CF22R14 possess and even higher IEC (2.35 ± 0.27 m*eq* g^{-1} in pristine state). Although, a more efficient ion transfer can be assumed with higher IEC, no improved MEC operation was found. This indicates that not the ionic capacity for cross-membrane ion transfer is the rate liming step in the present setup (observations presented in Section 3.1.) rather the membrane resistance per se seems limiting. During MEC operation (**Fig. 4.A**), each membrane underwent significant IEC decrease (-16.6 ± 1.0 % ($p = 0.0027$), -9.4 ± 0.4 % ($p = 0.011$) and -15.8 ± 1.2 % ($p = 0.014$) for FKE, PSEBS SU and CF22R14, respectively). Nevertheless, the re-activation was effective for all membrane materials (**Fig. 4.A**).

As for the EC operation, the determination of IEC values (**Fig. 4.B**) revealed further details. Substantial IEC decrease was found for each membrane after use, with -31 ± 1.7 %, -23.7 ± 1.9 % and -71.2 ± 17.6 % in case of the FKE, PSEBS SU and CF22R14, respectively ($p << 0.05$ in all cases). This means significantly higher IEC loss compared to the outcomes of MEC operation. Furthermore, even though a good IEC recovery could be achieved with the two homogeneous membranes after re-activation (87.9 ± 2.8 % for FKE and 85.3 ± 3.8 % for PSEBS SU), the pristine and re-activated mean IEC significantly differed ($p = 0.011$ and 0.0052). Consequently, the re-activation efficiency was also consistently lower compared to using the membranes for MEC (97.2 ± 1.1 % for FKE and 95 ± 1.8 % for PSEBS SU). Moreover, the CF22R14 membrane – in addition to the more severe deterioration of IEC after use – displayed less than 50 % (46.6 ± 4.4 %) recovery (**Fig. 4.B**).

Thus, in general the EC operation with higher current density caused more considerable alterations regarding λ and IEC of the studied IEMs than use in MEC. While the FKE and PSEBS SU homogeneous membranes could regain similarly ~ 85 % of the pristine λ and IEC values, the heterogeneous CF22R14 membrane reflected weaker re-activation efficiency, presumably due to the irreversible changes in the functional groups of the polymer.

It was shown previously that CEM may undergo severe alterations in terms of λ and IEC after use for electrochemical processes such as electrodialysis of complex samples [24]. Biological and chemical foulants (e.g. calcium-phosphate or large counter-ions with multiple charge) are usually underlined as main causes of membrane deterioration [24,48]. In addition, scaling – due to concentration polarization – may also have a great effect on fundamental membrane properties such as IEC. By studying Neosepta® ion exchange membranes, it was demonstrated that λ and IEC of CEM decrease as the membrane deteriorates, and in addition, the applied current density has an influence on the phenomenon [24,49]. The thickness of CEM is also reduced in long term. Our results are in good agreement with these findings, as for each applied CEM, both λ and IEC decreased after use in proportion to the current density range of MEC and EC operations.

3.3. Results of membrane polarization experiments

In order to assess the membrane properties under operation, their σ was determined (via membrane polarization tests). To provide a comprehensive insight, a set of parameters (c_{PBS}, c_{Ac} and initial electrolyte pH) representing the process window of BES operation was assessed using a design of experiment approach (**Table 1**).

The results of conductivity measurements for the PSEBS SU membrane used in MEC experiments are illustrated in **Fig. 5.A-F.** It is of note that the other two membrane materials provided similar responses pertaining to the trends and effects (Appendix, **Fig. A.2** and **Fig. A.3** for FKE and CF22R14, respectively). The polarization assays showed that the σ of the membranes (for the studied conditions) was independent of the initial pH and c_{Ac} (ANOVA indicated significant effect for $p = 0.01$ of the pH only in case of the pristine CF22R14). Nevertheless, c_{PBS} had a significant influence ($p < 0.05$ in all cases) on σ regardless of the membranes' actual condition ($p < 0.05$ in all cases). This is in line with the change of the electrolyte's ionic strength at different c_{PBS} as well as previous experiments and modelling of membranes [16,17].

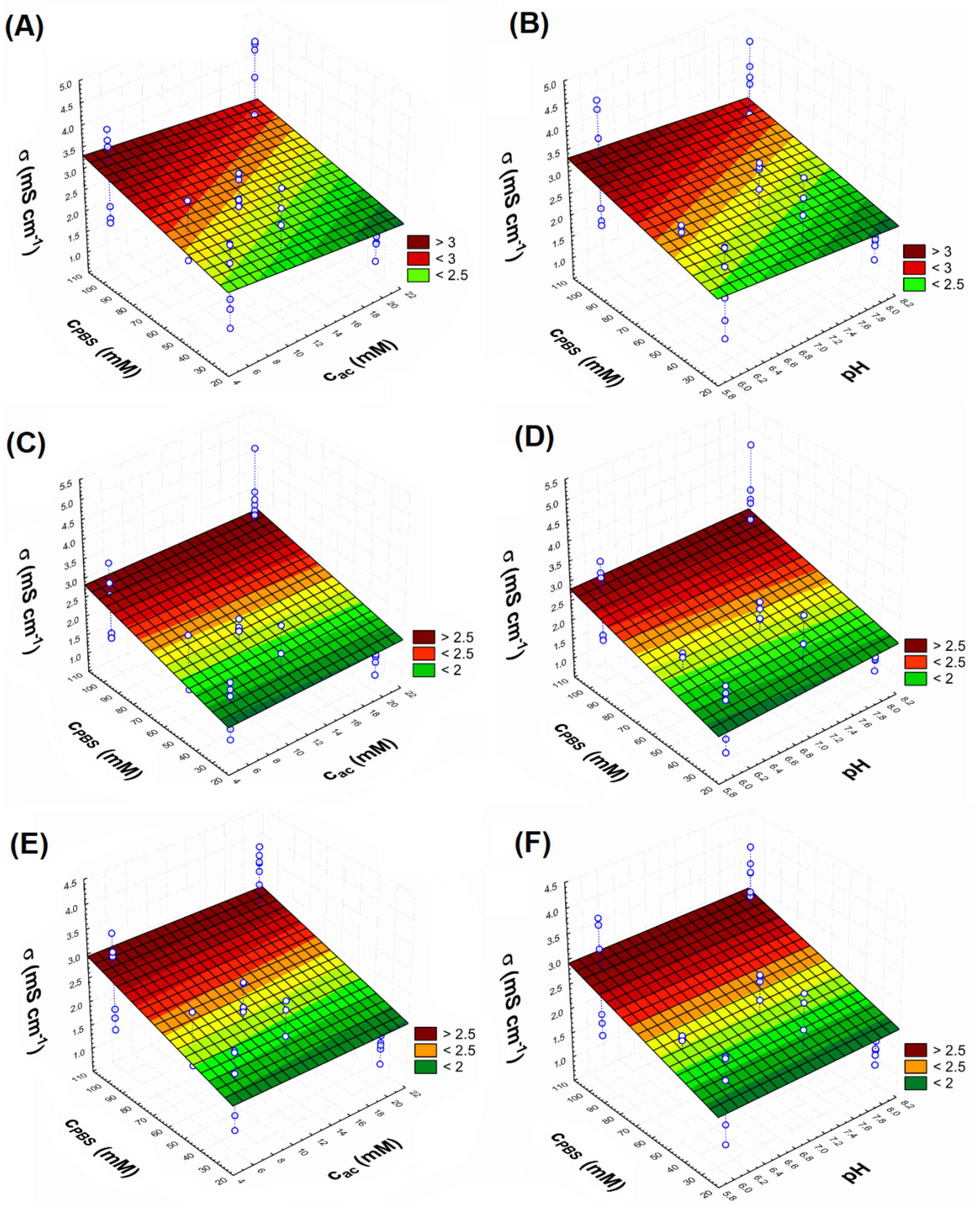

Fig. 5 – Ionic conductivity (σ) of PSEBS SU membrane as a function of the studied factors (MEC operation). A-B: pristine; C-D: used; E-F: re-activated (See Appendix, **Fig. A.2** and **Fig. A.3** for FKE and CF22R14, respectively).

The special importance of the electrolyte concentration and hence σ was underlined previously [16,32,50]. Since BES are usually operated with low-conductivity electrolyte solutions, only separators possessing sufficient σ at these low ion concentrations should be applied [14]. Accordingly, the σ of commercial materials being usually reported in 0.5 M NaCl/KCl do not provide a proper basis for screening of membranes. Considering the trends observed for the studied factors (PBS concentration, c_{Ac}, pH), only the PBS concentration was found to have a significant effect ($p < 0.05$ in all cases) on σ of the membranes in the given range, similarly to the MEC experiments. **Fig. 6.A-F** depicts the σ data of the experimental design and the fitted surface in case of PSEBS SU membrane. The trends for all membrane materials were uniform, and the results with FKE and CF22R14 membranes are shown in the Appendix (**Fig. A.4** and **Fig. A.5** for FKE and CF22R14, respectively).

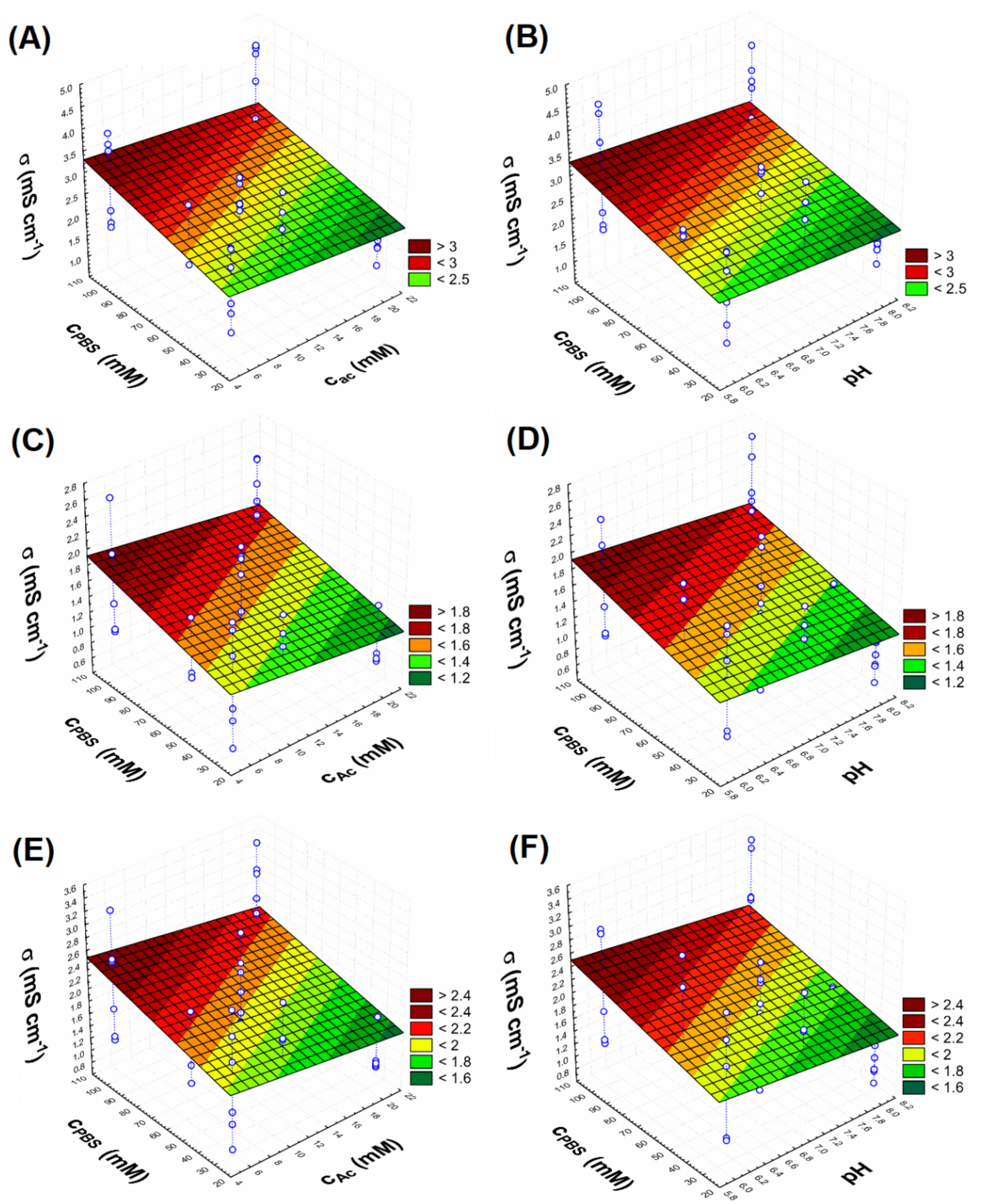

Fig. 6 – Ionic conductivity (σ) of PSEBS SU membrane as a function of the studied factors (EC operation). A-B: pristine; C-D: used; E-F: re-activated (See Appendix, **Fig. A.4** and **Fig. A.5** for FKE and CF22R14, respectively).

The effect of membrane usage and re-activation on σ was further evaluated considering the center points of the experimental design (pH = 7, c_{Ac} = 10 mM, c_{PBS} =

50 mM) with 9 parallel measurements per sample. The fundamental question to answer was whether the studied membrane materials were able to withstand sufficiently the environment of a microbial- or abiotic electrochemical system, while keeping their functional integrity. The previously discussed λ and IEC values indicated only minor alterations in case of MEC operation and a pronounced decrease in case of EC operation. Thus, it had to be assumed a similar trend for the conductivity, as well. Indeed, when using the membranes in MEC mode, slight changes appeared (**Fig. 7.A**). The σ of FKE membrane shows the lowest decrease, from 0.63 ± 0.09 mS cm^{-1} before to 0.55 ± 0.09 mS cm^{-1} after EC operation, i.e. -13 ± 1.9 % ($p = 0.136$) compared to the pristine value. The re-activation resulted in a sufficient retrieval of σ up to 92 ± 7.2 % of the initial σ. The PSEBS SU membrane reveals the highest pristine conductivity of 2.71 ± 0.61 mS cm^{-1}, even though a -20.3 ± 4.5 % ($p = 0.095$) decrease occurred. After re-activation, 86.6 ± 9.6 % of the pristine conductivity could be restored (2.35 ± 0.52 mS cm^{-1}). The heterogeneous CF22R14 membrane also reflected good pristine conductivity (1.04 ± 0.18 mS cm^{-1}), which decreased significantly after use by -22.6 ± 3.6 % ($p = 0.0097$), down to 0.80 ± 0.12 mS cm^{-1}. Nevertheless, the re-activation was successful also in case of this material, leading to 92.6 ± 5.6 % regain of conductivity (0.96 ± 0.16 mS cm^{-1}).

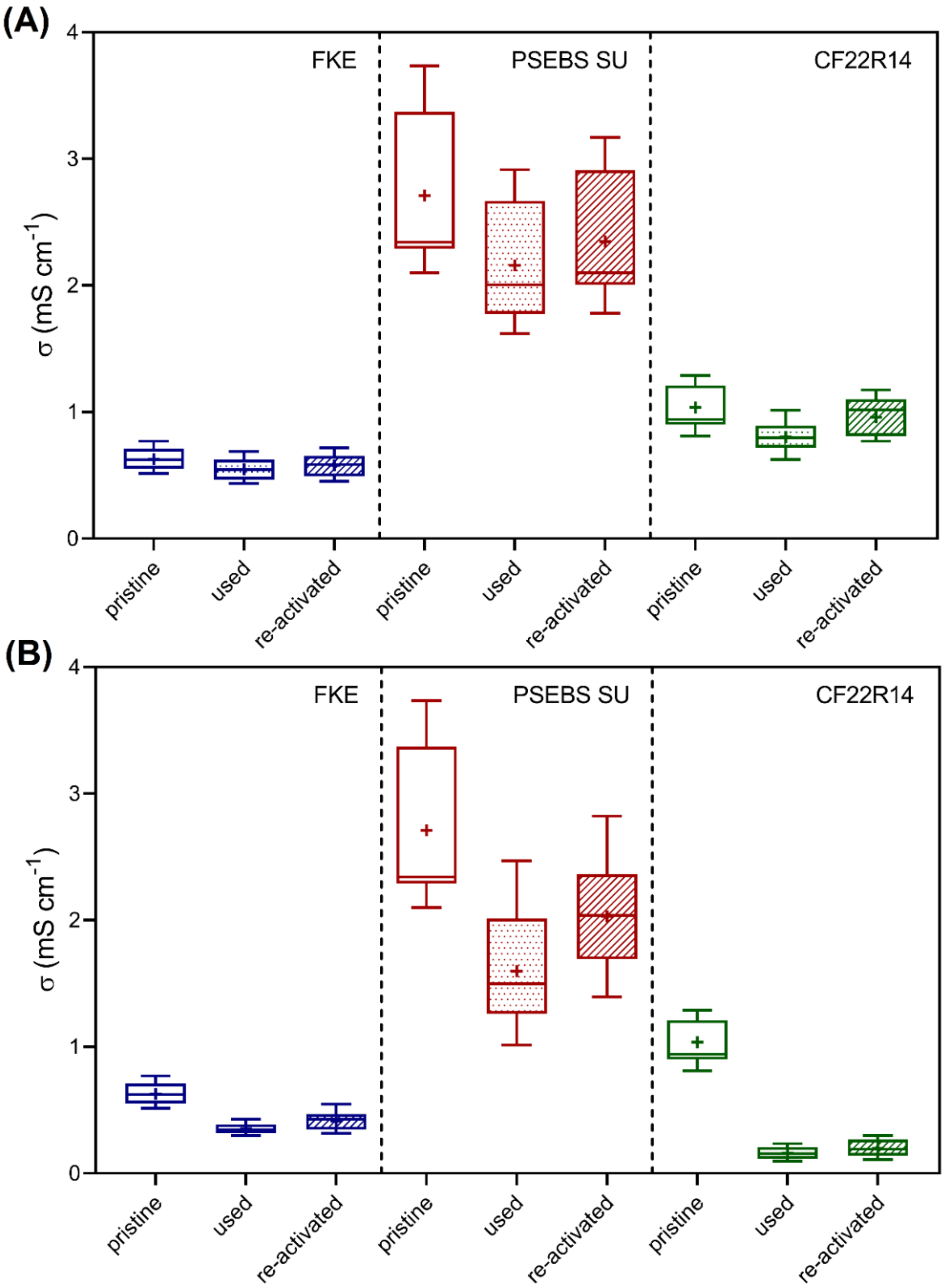

Fig. 7 – Box plots for ionic conductivity (σ) of FKE, PSEBS SU and CF22R14 samples at pH = 7, c_{Ac} = 10 mM, c_{PBS} = 50 mM. (A) – MEC operation; (B) – EC operation. Boxes indicate 95 % CI, whiskers present minimum and maximum values, while horizontal lines and cross symbols present median and mean, respectively.

Compared to the MEC results, the loss of σ during EC operation was more pronounced, while the re-activation efficiency was lower for each membrane sample. The 10 days long EC operation caused an average of -44 ± 2.7, -41 ± 6.4 and -84 ± 12.7 % decrease of σ ($p << 0.05$ in all cases) in case of FKE, PSEBS SU and CF22R14 membranes, respectively (**Fig. 7.B**). In addition to the higher losses compared to MEC operation, the main observation for EC operation is the significantly limited re-activation for each sample. Among them, PSEBS SU showed the best σ retrieval (74.9 ± 8.1 % of the pristine value), followed by the FKE (65.6 ± 6.1 %) and CF22R14 (19.2 ± 3.3 %).

It was shown that in case of CEMs used in electrodialysis, the deterioration of the membranes through the loss of sulfonic acid functional groups led to highly reduced counter-ion mobility and concentration in the internal membrane phase, which eventually decreases σ [24]. Based on the above presented results we assume that this phenomenon was observed in our experiments, as well. On the one hand, the σ results are in good agreement with the data obtained from λ and IEC measurements, indicating that the heterogeneous membrane was most affected by the operation under increased current density. On the other hand, the generally higher stress caused by the higher current density implies the potential need of additional re-activation strategies (e.g. soaking solution optimization, elevated temperature treatment, contact time, etc.) to further increase the efficiency of regaining pristine membranes properties. Considering operation times up to months/year, the effects deteriorating the membranes' operational stability (e.g. more severe chemical or biofouling) can become even more pronounced, which underlines the importance of regular re-activation periods. Thus, in-place re-activation techniques are required for scaled-up applications.

3.4. Structural properties of the CEMs after operation

Concerning microscopic structural integrity, the homogeneous CEMs seemed to be sufficiently stable. As for the FKE membrane, after use in MEC, no observable structural alteration could be seen (**Fig. 8.A**). Similarly, aside from a negligible undulated deformation of the membrane surface (**Fig. 8.B**), the PSEBS SU did not suffer structural damage during its usage in MEC operation. However, in case of CF22R14 CEM the presence of a few pinholes with a diameter of ~30 - 50 μm was observed (**Fig. 8.C-D**).

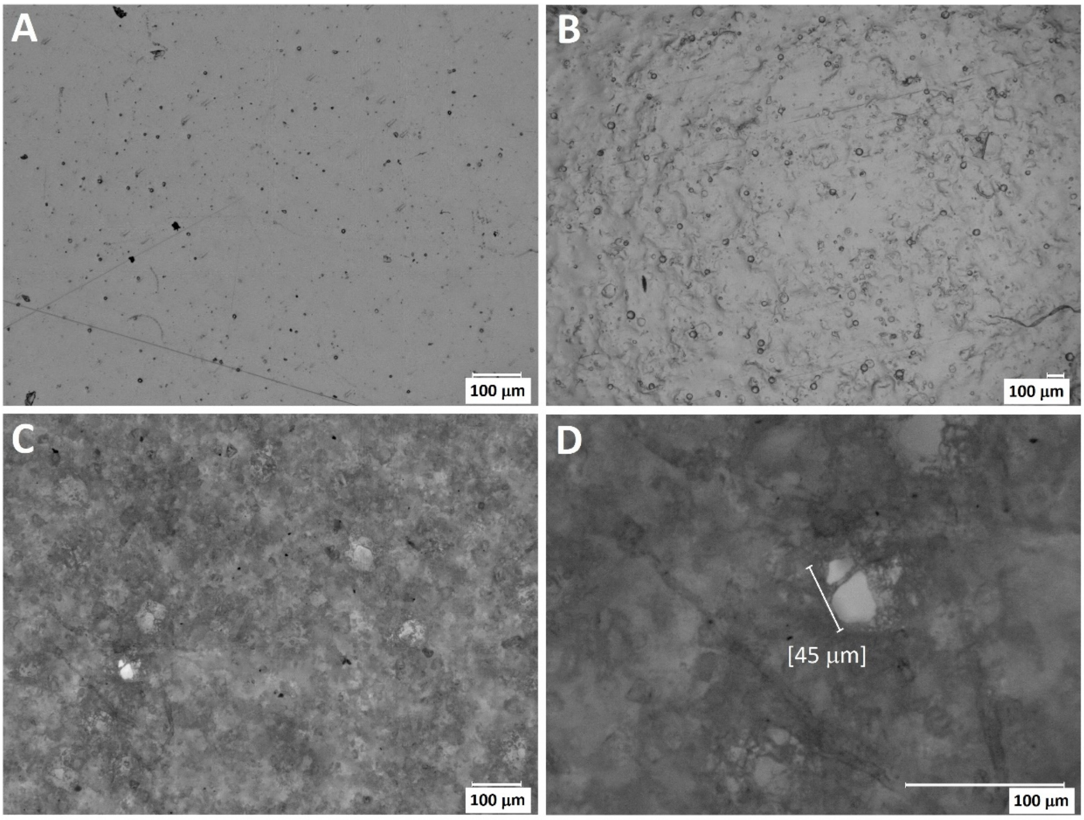

Fig. 8 – Optical images of used CEM samples from MEC operation. A: FKE; B: PSEBS SU; C-D: CF22R14

During EC operation, FKE and PSEBS SU demonstrated similar structural stability, while only minor undulation was observed for the PSEBS SU membrane (**Fig. 9.A-B**). However, the used CF22R14 was covered with a large number of pinholes of different sizes (35 – 116.5 μm) (**Fig. 9.C-D**). Moreover, considering also the findings of MEC operation, the number and the size range of the formed pinholes seemed to be proportional to the applied current density.

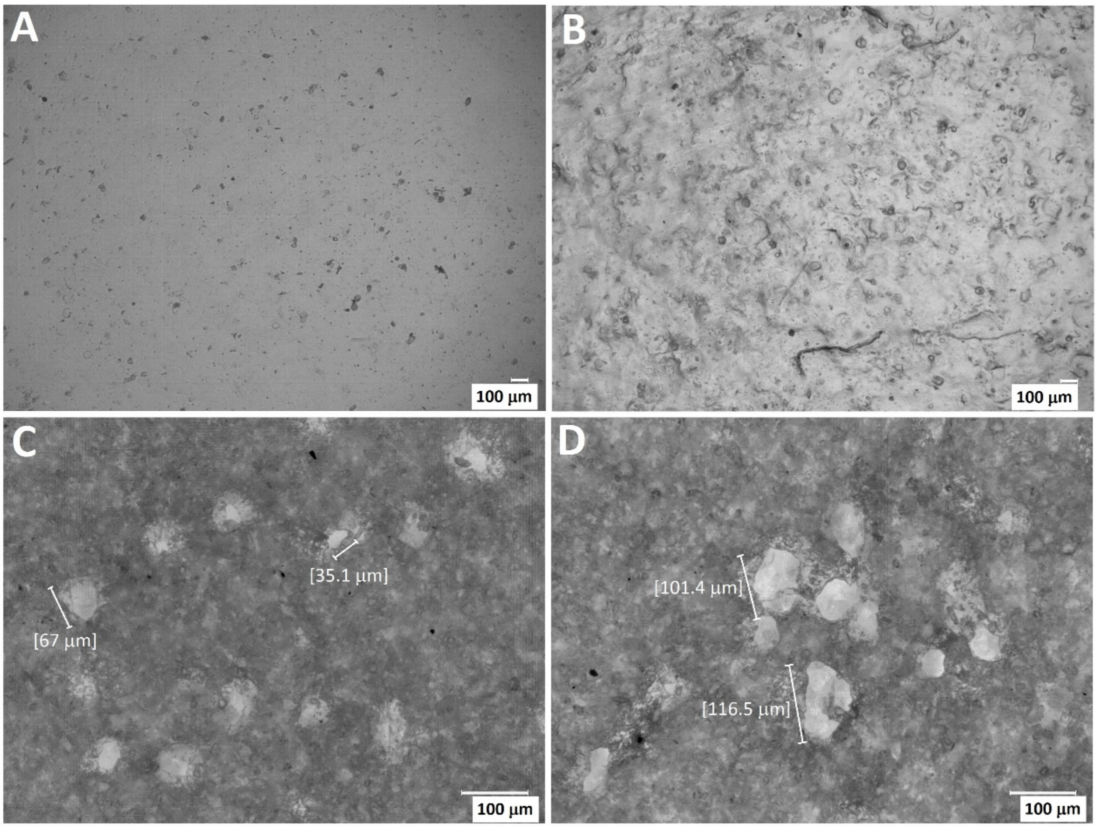

Fig. 9 – Optical images of used CEM samples from EC operation. A: FKE; B: PSEBS SU; C-D: CF22R14

The mechanism of pinhole formation – due to the loss of ion exchange resin dispersed in the polymer – is an interesting aspect needing further investigation in order to improve the membrane preparation process. Although several chemical / biological factors interfere with the membrane material, the reason causing the deterioration is presumably the inhomogeneous current density distribution over the membrane due to the heterogeneous structure of the CF22R14 forming ionically conducting and non-conducting regions. The finding that the amount and size of the formed pinholes was a function of *i* further supports the assumption that the pinhole formation can be attributed to the inhomogeneous current density distribution over the membrane surface. Due to this phenomenon, pronounced concentration polarization occurs mainly at higher current densities, and in addition, 'membrane erosion' driven by electroconvective forces may develop at the membrane surface [51]. Increased swelling of a membrane – as it was observed also in case of CF22R14 – may also lead to structural deterioration, such as cavity formation [24]. In case of FKE and PSEBS SU membranes, the inherent potential of the aforementioned strategies for enhancing the re-activation efficiency is further underlined in the light of the above results, as they apparently did not undergo severe integrity changes during operation.

Conclusions

This work presents alterations of λ, IEC and σ of three different IEM (i.e. FKA, PSEBS SU CEM and CF22R14) when applied in MEC and EC operation modes in the short-term (10 days). Operation at low $i_{\max}$ systematically resulted in less changes of the studied parameters compared to high $i_{\max}$. Although chemical re-activation was sufficient for regaining nearly pristine λ, IEC and σ values for each CEM after use in MEC, the higher applied current density in EC operation induced significant and, mainly in the case of CF22R14, irreversible reduction of the examined parameters. Investigating the effect of initial electrolyte pH, c_{Ac} and c_{PBS} on σ showed c_{PBS} to be the sole parameter with significant influence, considering factor ranges relevant to BES.

Overall, it was clearly demonstrated that the experimental PSEBS SU CEM has sufficient material properties (λ, IEC, σ) accompanied by excellent operational and structural stability and re-activation ability compared to commercial materials, such as the FKE. The heterogeneous CF22R14 turned out to be the least stable membrane, as indicated not only by the high alteration and lower re-activation efficiency of λ, IEC and σ, but also by formation of pinholes in the membrane. While the FKE and PSEBS SU kept their integrity, the amount and size of the formed pinholes in CF22R14 increased with the current density. The outcomes of a 10-day-long MEC and EC operation revealed notable changes in all examined parameters (λ, IEC, σ), which indicates the need for further studies with extended duration and mechanistic investigation to understand potential functional stability alterations in long-term operation. Based on the positive outcomes of this study, follow-up research may focus on the benchmarking of PSEBS SU in additional abiotic and microbial electrochemical technologies, such as microbial or pure electrochemical desalination cells.

Acknowledgements

L. K. acknowledges support given by the DAAD (Short-Term Research Grant, 57442045). Supported by the ÚNKP-21-4 New National Excellence Program of the Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund. This research work was supported by the project entitled "Establishment of a National Multidisciplinary Laboratory for Climate Change", No. NKFIH-471-3/2021 by the government of Hungary. This work was supported by the Helmholtz-Association in the frame of the Integration Platform “Tapping nature’s potential for sustainable production and a healthy environment” at the UFZ.

References

[1] H. Strathmann, Ion-Exchange Membrane Separation Processes, Elsevier, Amsterdam, 2004.

[2] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications, Desalination. 264 (2010) 268–288. doi:10.1016/j.desal.2010.04.069.

[3] J.W. Post, H.V.M. Hamelers, C.J.N. Buisman, Energy recovery from controlled mixing salt and fresh water with a reverse electrodialysis system, Environmental Science and Technology. 42 (2008) 5785–5790. doi:10.1021/es8004317.

[4] A. Grabowski, G. Zhang, H. Strathmann, G. Eigenberger, The production of high purity water by continuous electrodeionization with bipolar membranes: Influence of the anion-exchange membrane permselectivity, Journal of Membrane Science. 281 (2006) 297–306. doi:10.1016/j.memsci.2006.03.044.

[5] M. Igawa, K. Echizenya, T. Hayashita, M. Seno, Donnan Dialysis Desalination, Chemistry Letters. 15 (1986) 237–238. doi:10.1246/cl.1986.237.

[6] K. Sopian, W.R. Wan Daud, Challenges and future developments in proton exchange membrane fuel cells, Renewable Energy. 31 (2006) 719–727. doi:10.1016/j.renene.2005.09.003.

[7] M.Y. Kariduraganavar, R.K. Nagarale, A.A. Kittur, S.S. Kulkarni, Ion-exchange membranes: preparative methods for electrodialysis and fuel cell applications, Desalination. 197 (2006) 225–246. doi:10.1016/j.desal.2006.01.019.

[8] Q. Wen, Y. Wu, D. Cao, L. Zhao, Q. Sun, Electricity generation and modeling of microbial fuel cell from continuous beer brewery wastewater, Bioresource Technology. 100 (2009) 4171–4175. doi:10.1016/j.biortech.2009.02.058.

[9] H. Liu, B.E. Logan, Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane, Environmental Science and Technology. 38 (2004) 4040–4046. doi:10.1021/es0499344.

[10] H. Wang, Z.J. Ren, A comprehensive review of microbial electrochemical systems as a platform technology, Biotechnology Advances. 31 (2013) 1796–1807. doi:10.1016/j.biotechadv.2013.10.001.

[11] U. Schröder, F. Harnisch, L.T. Angenent, Microbial electrochemistry and technology: Terminology and classification, Energy and Environmental Science. 8 (2015) 513–519. doi:10.1039/c4ee03359k.

[12] M.I. San-Martín, F.J. Carmona, R.M. Alonso, P. Prádanos, A. Morán, A. Escapa, Assessing the ageing process of cation exchange membranes in bioelectrochemical systems, International Journal of Hydrogen Energy. 44 (2019) 25287–25296. doi:10.1016/j.ijhydene.2019.08.004.

[13] L. Koók, G. Dörgő, P. Bakonyi, T. Rózsenberszki, N. Nemestóthy, K. Bélafi-Bakó, J. Abonyi, Directions of membrane separator development for microbial fuel cells: A retrospective analysis using frequent itemset mining and descriptive statistical approach, Journal of Power Sources. 478 (2020). doi:10.1016/j.jpowsour.2020.229014.

[14] B.R. Dhar, H.S. Lee, Membranes for bioelectrochemical systems: challenges and research advances, Environmental Technology (United Kingdom). 34 (2013) 1751–1764. doi:10.1080/09593330.2013.822007.

[15] R.A. Rozendal, H.V.M. Hamelers, C.J.N. Buisman, Effects of membrane cation transport on pH and microbial fuel cell performance, Environmental Science and Technology. 40 (2006) 5206–5211. doi:10.1021/es060387r.

[16] F. Harnisch, U. Schröder, F. Scholz, The suitability of monopolar and bipolar ion exchange membranes as separators for biological fuel cells, Environmental Science and Technology. 42 (2008) 1740–1746. doi:10.1021/es702224a.

[17] F. Harnisch, R. Warmbier, R. Schneider, U. Schröder, Modeling the ion transfer and polarization of ion exchange membranes in bioelectrochemical systems, Bioelectrochemistry. 75 (2009) 136–141. doi:10.1016/j.bioelechem.2009.03.001.

[18] F. Harnisch, U. Schröder, Selectivity versus mobility: Separation of anode and cathode in microbial bioelectrochemical systems, ChemSusChem. 2 (2009) 921–926. doi:10.1002/cssc.200900111.

[19] L. Koók, P. Bakonyi, F. Harnisch, J. Kretzschmar, K.J. Chae, G. Zhen, G. Kumar, T. Rózsenberszki, G. Tóth, N. Nemestóthy, K. Bélafi-Bakó, Biofouling of membranes in microbial electrochemical technologies: Causes, characterization methods and mitigation strategies, Bioresource Technology. 279 (2019) 327–338. doi:10.1016/j.biortech.2019.02.001.

[20] V. Mavrov, W. Pusch, O. Kominek, S. Wheelwright, Concentration polarization and water splitting at electrodialysis membranes, Desalination. 91 (1993) 225–252. doi:10.1016/0011-9164(93)80062-R.

[21] S.M. Hosseini, S.S. Madaeni, A.R. Khodabakhshi, The electrochemical characterization of ion exchange membranes in different electrolytic environments: Investigation of concentration and pH effects, Separation Science and Technology. 47 (2012) 455–462. doi:10.1080/01496395.2011.615046.

[22] B. Kokabian, V.G. Gude, Role of membranes in bioelectrochemical systems, Membrane Water Treatment. 6 (2015) 53–75. doi:10.12989/mwt.2015.6.1.053.

[23] S.M. Daud, B.H. Kim, M. Ghasemi, W.R.W. Daud, Separators used in microbial electrochemical technologies: Current status and future prospects, Bioresource Technology. 195 (2015) 170–179. doi:10.1016/j.biortech.2015.06.105.

[24] R. Ghalloussi, W. Garcia-Vasquez, L. Chaabane, L. Dammak, C. Larchet, S. V. Deabate, E. Nevakshenova, V. Nikonenko, D. Grande, Ageing of ion-exchange membranes in electrodialysis: A structural and physicochemical investigation, Journal of Membrane Science. 436 (2013) 68–78. doi:10.1016/j.memsci.2013.02.011.

[25] J.H. Choi, S.H. Moon, Structural change of ion-exchange membrane surfaces under high electric fields and its effects on membrane properties, Journal of Colloid and Interface Science. 265 (2003) 93–100. doi:10.1016/S0021-9797(03)00136-X.

[26] C. Jiang, D. Zhang, A.S. Muhammad, M.M. Hossain, Z. Ge, Y. He, H. Feng, T. Xu, Fouling deposition as an effective approach for preparing monovalent selective membranes, Journal of Membrane Science. 580 (2019) 327–335. doi:10.1016/j.memsci.2019.03.035.

[27] N.P. Berezina, N.A. Kononenko, O.A. Dyomina, N.P. Gnusin, Characterization of ion-exchange membrane materials: Properties vs structure, Advances in Colloid and Interface Science. 139 (2008) 3–28. doi:10.1016/j.cis.2008.01.002.

[28] P. Choi, N.H. Jalani, R. Datta, Thermodynamics and Proton Transport in Nafion, Journal of The Electrochemical Society. 152 (2005) E84–E89. doi:10.1149/1.1855872.

[29] J.C. Díaz, J. Kamcev, Ionic conductivity of ion-exchange membranes: Measurement techniques and salt concentration dependence, Journal of Membrane Science. 618 (2021) 118718. doi:10.1016/j.memsci.2020.118718.

[30] M. Shabani, H. Younesi, M. Pontié, A. Rahimpour, M. Rahimnejad, A.A. Zinatizadeh, A critical review on recent proton exchange membranes applied in microbial fuel cells for renewable energy recovery, Journal of Cleaner Production. 264 (2020) 121446. doi:10.1016/j.jclepro.2020.121446.

[31] N. Dizge, B.O. Unal, E.B. Arikan, A. Karagunduz, B. Keskinler, Recent progress and developments in membrane materials for microbial electrochemistry technologies: A review, Bioresource Technology Reports. 8 (2019) 100308. doi:10.1016/j.biteb.2019.100308.

[32] L. Koók, J. Zitka, S. Szakács, T. Rózsenberszki, M. Otmar, N. Nemestóthy, K. Bélafi-Bakó, P. Bakonyi, Efficiency, operational stability and biofouling of novel sulfomethylated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene cation exchange membrane in microbial fuel cells, Bioresource Technology. 333 (2021) 125153. doi:10.1016/j.biortech.2021.125153.

[33] R. Cardeña, L. Koók, J. Žitka, P. Bakonyi, B. Galajdová, M. Otmar, N. Nemestóthy, G. Buitrón, Evaluation and ranking of polymeric ion exchange membranes used in microbial electrolysis cells for biohydrogen production, Bioresource Technology. 319 (2021) 124182. doi:10.1016/j.biortech.2020.124182.

[34] M. Otmar, J. Gaálová, J. Žitka, L. Brožová, P. Cuřínová, M. Kohout, Š. Hovorka, J.E. Bara, B. Van der Bruggen, J. Jirsák, P. Izák, Preparation of PSEBS membranes bearing (S)-(−)-methylbenzylamine as chiral selector, European Polymer Journal. 122 (2020) 109381. doi:10.1016/j.eurpolymj.2019.109381.

[35] L. Brožová, J. Křivčík, D. Neděla, V. Kysela, J. Žitka, The influence of activation of heterogeneous ion-exchange membranes on their electrochemical

properties, Desalination and Water Treatment. 56 (2015) 3228–3232. doi:10.1080/19443994.2014.980975.

[36] W. Garcia-Vasquez, R. Ghalloussi, L. Dammak, C. Larchet, V. Nikonenko, D. Grande, Structure and properties of heterogeneous and homogeneous ion-exchange membranes subjected to ageing in sodium hypochlorite, Journal of Membrane Science. 452 (2014) 104–116. doi:10.1016/j.memsci.2013.10.035.

[37] B.H. Kim, H.S. Park, H.J. Kim, G.T. Kim, I.S. Chang, J. Lee, N.T. Phung, Enrichment of microbial community generating electricity using a fuel-cell-type electrochemical cell, Applied Microbiology and Biotechnology. 63 (2004) 672–681. doi:10.1007/s00253-003-1412-6.

[38] P. Długołecki, K. Nymeijer, S. Metz, M. Wessling, Current status of ion exchange membranes for power generation from salinity gradients, Journal of Membrane Science. 319 (2008) 214–222. doi:10.1016/j.memsci.2008.03.037.

[39] P. Bakonyi, L. Koók, G. Kumar, G. Tóth, T. Rózsenberszki, D.D. Nguyen, S.W. Chang, G. Zhen, K. Bélafi-Bakó, N. Nemestóthy, Architectural engineering of bioelectrochemical systems from the perspective of polymeric membrane separators: A comprehensive update on recent progress and future prospects, Journal of Membrane Science. 564 (2018) 508–522. doi:10.1016/j.memsci.2018.07.051.

[40] G. Inzelt, A. Lewenstam, F. Scholz, Handbook of reference electrodes, 2013. doi:10.1007/978-3-642-36188-3.

[41] J. Hnát, M. Plevová, J. Žitka, M. Paidar, K. Bouzek, Anion-selective materials with 1,4-diazabicyclo[2.2.2]octane functional groups for advanced alkaline water electrolysis, Electrochimica Acta. 248 (2017) 547–555. doi:10.1016/j.electacta.2017.07.165.

[42] G.M. Geise, M.A. Hickner, B.E. Logan, Ionic resistance and permselectivity tradeoffs in anion exchange membranes, ACS Applied Materials and Interfaces. 5 (2013) 10294–10301. doi:10.1021/am403207w.

[43] J.R. Boston, T.E. Rudy, J.A. Kubinski, Multiple statistical comparisons: Fishing with the right bait, Journal of Critical Care. 6 (1991). doi:10.1016/0883-9441(91)90021-K.

[44] A.K. Luther, J. Desloover, D.E. Fennell, K. Rabaey, Electrochemically driven extraction and recovery of ammonia from human urine, Water Research. 87 (2015) 367–377. doi:10.1016/j.watres.2015.09.041.

[45] M.E.R. Christiaens, S. Gildemyn, S. Matassa, T. Ysebaert, J. De Vrieze, K. Rabaey, Electrochemical Ammonia Recovery from Source-Separated Urine for Microbial Protein Production, Environmental Science and Technology. 51 (2017) 13143–13150. doi:10.1021/acs.est.7b02819.

[46] V. Yadav, A. Rajput, N.H. Rathod, V. Kulshrestha, Enhancement in proton conductivity and methanol cross-over resistance by sulfonated boron nitride composite sulfonated poly (ether ether ketone) proton exchange membrane, International Journal of Hydrogen Energy. 45 (2020) 17017–17028. doi:10.1016/j.ijhydene.2019.06.091.

[47] A.E. Kozmai, V. V. Nikonenko, S. Zyryanova, N.D. Pismenskaya, L. Dammak, L. Baklouti, Modelling of anion-exchange membrane transport properties with taking into account the change in exchange capacity and swelling when varying bathing solution concentration and pH, Journal of Membrane Science. 590 (2019) 117291. doi:10.1016/j.memsci.2019.117291.

[48] Y. Tanaka, Ion Exchange Membranes: Fundamentals and Applications: Second Edition, 2015. doi:10.1016/C2013-0-12870-X.

[49] E. Korngold, F. de Körösy, R. Rahav, M.F. Taboch, Fouling of anionselective membranes in electrodialysis, Desalination. 8 (1970) 195–220. doi:10.1016/S0011-9164(00)80230-1.

[50] M. Oliot, S. Galier, H. Roux de Balmann, A. Bergel, Ion transport in microbial fuel cells: Key roles, theory and critical review, Applied Energy. 183 (2016) 1682–1704. doi:10.1016/j.apenergy.2016.09.043.

[51] N.D. Pismenskaya, V. V. Nikonenko, N.A. Melnik, K.A. Shevtsova, E.I. Belova, G. Pourcelly, D. Cot, L. Dammak, C. Larchet, Evolution with time of hydrophobicity and microrelief of a cation-exchange membrane surface and its impact on overlimiting mass transfer, Journal of Physical Chemistry B. 116 (2012) 2145–2161. doi:10.1021/jp2101896.