

Post-print: L. Gurreri, A. Filingeri, M. Ciofalo, A. Cipollina, M. Tedesco, A. Tamburini, G. Micale, *Electrodialysis with asymmetrically profiled membranes: influence of profiles geometry on desalination performance and limiting current phenomena*, Desalination, 506 (2021) 115001, <https://doi.org/10.1016/j.desal.2021.115001>

Electrodialysis with asymmetrically profiled membranes: influence of profiles geometry on desalination performance and limiting current phenomena

Luigi Gurreri^a, Antonia Filingeri^a, Michele Ciofalo^a, Andrea Cipollina^{a*}, Michele Tedesco^b,
Alessandro Tamburini^a, Giorgio Micale^a

^a *Department of Engineering, University of Palermo, Viale delle Scienze ed. 6, 90128 Palermo, Italy*

^b *Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911 MA Leeuwarden, the Netherlands*

*corresponding author – email: andrea.cipollina@unipa.it

ABSTRACT

Electrodialysis (ED) has recently gained much attention in the wide field of desalination and water treatment. However, energy consumption and capital costs may impair the process competitiveness. In this regard, limiting current density (LCD) and current efficiency (η) are key performance parameters for optimized ED systems. In this work, an experimental campaign was carried out characterizing the performance of ED stacks when adopting asymmetrically profiled membranes. Current–voltage curves were recorded under different operating conditions mimicking the operation of brackish water or seawater desalination units. Results showed that there was a preferable direction of the electric current relative to the membrane profiles, which provided higher values of LCD and of maximum η . Stacks with Overlapped Crossed Filaments profiled membranes performed better than conventional ED stacks with flat membranes and spacers by increasing the LCD (by ~20% under various operating conditions) and the maximum η (e.g., from ~55–65% to ~70–73% at 0.5-60 g/l inlet concentrations). The specific energy consumption was significantly reduced (even more than 50%). On the contrary, the investigated pillar-profiled membranes exhibited the worst performances.

24 The present results suggest that well-designed profiled membranes can reduce the costs of
25 desalination via ED.

26 **Keywords:** ion exchange membrane; corrugated membrane; current utilization; polarisation
27 phenomena; mass transport.

28 **1 Introduction**

29 Electrodialysis (ED) is an electro-membrane process that exploits the selective transport of ions
30 through ion-exchange membranes under the effect of an applied electric field in order to produce two
31 streams at different concentration [1–3]. A number of different configurations of ED units have been
32 studied for applications in food processing, biotechnology, and pharmaceutical industry [4–6]. Many
33 studies have been conducted on the treatment of wastewater from several sources [7]. However, the
34 main industrial application of ED is saline water desalination. ED covers ~2% of the global
35 desalination capacity, with low to medium size plants (capacity typically below 10,000 m³/day) [8,9]
36 and electrical energy consumption in the range 2-5 kWh/m³ [10]. ED has gained a main role in the
37 market of brackish water desalination, where the small desalination rate required makes ED
38 competitive compared to Reverse Osmosis (RO). There are some applications of ED to treat seawater
39 for table salt production [3]. However, drinking water production from seawater is not yet
40 competitive, thus only pilot plants have been so far installed and operated [11]. High costs are due to
41 the loss of selectivity encountered with high concentration gradients and to the higher membrane area
42 [12]. On the other hand, research is currently addressing the challenge of developing competitive ED
43 systems for the desalination of concentrated solutions (e.g. brines [7]). In particular, both modelling
44 [13–16] and experimental [17–19] studies have been conducted on ED desalination of seawater. The
45 use of multi-stage ED systems with a suitable distribution of membrane area (decreasing in
46 consecutive stacks) allowed for a reduction of the energy consumption up to 2.2 kWh/m³ for
47 desalinating a 0.51 M NaCl solution to 0.0054 M [19]. This promising result was obtained by using

membranes with low permeability to water and operating at current densities up to 95% of the LCD, thus increasing current efficiency and water recovery.

Current efficiency (η) and limiting current density (LCD) are key operating parameters of ED stacks. The current efficiency depends on the selectivity and transport properties of the membranes, and is affected by salt back-diffusion and water flux via osmosis and electro-osmosis [20–23]. LCD depends on the transport mechanisms in solution (especially in the diluate compartment) and in membrane [1,24,25]. Both η and LCD are significantly affected by the channel geometry. The existence of the LCD results from concentration polarization phenomena [26]. From the Nernst film theory [27–29], under the assumption of local electroneutrality and for a binary electrolyte, the limiting current density associated to a null concentration at the membrane on the depleted solution side is [1]:

$$LCD = \frac{z_i F Sh D}{d_h (t_{IEM,i} - t_i)} C_{bulk,i} \quad (1)$$

where the subscript i indicates one ionic species (i.e., either anion or cation), z_i is the valence, F is the Faraday constant, Sh is the Sherwood number (mass transfer characteristics in the diluate), D is the salt diffusion coefficient in the solution, d_h is the hydraulic diameter (e.g. twice the channel thickness, $2H$), $t_{IEM,i}$ and t_i are the transport numbers in membrane and solution, respectively, and C_{bulk} is the bulk concentration in the diluate compartment. However, current–voltage curves exhibit three regions [1,3] with an overlimiting regime for both simple electro-membrane systems [30,31] and for ED stacks [32–35]. Overlimiting currents can be explained only partially by the formation of charge carriers via water dissociation (H^+ and OH^-) [36,37]. Electroconvection, instead, can be the main overlimiting mechanism involving the transport of salt ions [31,38,39]. Non-equilibrium electroconvection occurs through the development of an extended space charge region near the membrane and inhomogeneous electric fields causing dynamic vortices [40–43]. Overlimiting mechanisms and i – V curves are affected by membrane surface properties, such as the heterogeneity

71 of conductivity and surface geometry [44–48], as well as roughness, grade of hydrophobicity, and
72 superficial charge density [24,30,49,50].

73 The understanding of phenomena affecting LCD and the i – V behaviour is of fundamental importance
74 to prevent the drastic increase of the stack resistance and water dissociation that can lead to scaling
75 or fouling. Moreover, stacks and operating conditions providing higher LCD values offer the
76 possibility of desalinating with reduced membrane area and, thus, reduced investment costs [3]. The
77 LCD is conventionally assumed as a practical threshold for operating ED units. On the other hand,
78 recent studies have focused on overlimiting regimes enhancing mass transfer [38,51]. In all cases, the
79 LCD and the limiting behaviour of the stack are crucial to enhance the process efficiency.

80 Stack design and membrane surface properties affect the LCD in ED, and novel stack and IEM
81 designs can be exploited to enhance the ED performance in the limiting region. In this regard, a
82 promising ED development is the use of profiled (or corrugated) membrane, which allow ED stacks
83 to be assembled without separated spacers. Profiled membranes are provided with ion conductive
84 ridges, pillars or reliefs, designed to create the solution compartment [1,3]. Depending on the profiles
85 shape and on the operating conditions, profiled membranes may lead to several advantages over
86 conventional configurations with flat membranes and spacers [52]: lower electrical resistance, higher
87 active area, lower water splitting thanks to lower local current densities [31], reduction of
88 concentration polarization and increase of LCD (when proper geometries enhancing mixing are
89 adopted), facilitation of electroconvection, and lower pressure drop.

90 Larchet et al. [51] showed that profiled membranes increased mass transfer in ED units operated at
91 high electric currents (including overlimiting currents), resulting in a larger range of inlet
92 concentration in which high desalination rates were obtained, and reduced the hydraulic resistance.
93 Strathmann [3] reported ED experiments performed with profiled membranes with trapezoidal cross-
94 section profiles, which increased the active area by over 40%. The stack with profiled membranes
95 exhibited lower resistances and higher LCDs, yielding a higher desalination rate at any voltage.

96 Balster et al. [53] found an increase of LCD of more than 30% and a reduction of electrical resistance
97 by using profiled membranes. Zhao et al. [54] tested different notched membranes, which exhibited
98 higher desalination rates and a LCD increase of up to three times. Melnikov et al. [55] tested profiled
99 membranes in ED for the desalination of secondary steam condensate from ammonium nitrate
100 production. The stack with profiled membranes provided higher values of η and LCD, while
101 suppressing water dissociation [55]. Pressure drop is strongly affected by the profiles geometry, and
102 both experiments [56] and simulations [57] showed that the hydraulic resistance may be reduced by
103 simple profile-filled channels. Numerical simulations based on mathematical models confirmed the
104 possibility to enhance the performance of electro-membrane processes by using profiled IEMs
105 [58,59].

106 Another possible advantage of profiled membranes may be a reduction of fouling phenomena.
107 Fouling is one of the main issues of membrane processes. Various mechanisms can be involved in
108 both the reversible and irreversible fouling of IEMs [60], causing a variety of detrimental effects,
109 including higher membranes resistance, channel clogging, higher pressure drop and lower current
110 efficiency. Many research efforts are being made to characterize fouling, prepare anti-fouling
111 membranes, and propose prevention and cleaning strategies [60–62]. However, to the best of the
112 authors' knowledge, no studies on fouling in ED processes with profiled membranes have been
113 performed. Vermaas et al. [63] used natural seawater and river water in reverse electrodialysis
114 operations of 25 days after only 20 μm filtering pre-treatment, observing severe fouling issues.
115 However, profiled membranes with parallel ridges exhibited a slower increase of pressure drop and
116 a lower increase of ohmic resistance compared to flat membranes assembled with woven spacers, due
117 to lower colloidal trapping, organic fouling and preferential channeling. An anti-fouling strategy
118 combining feedwater switch and air sparging was proposed [64].

119 Despite the increasing interest in profiled membranes for ED, the effect of profile geometry on LCD
120 is still unknown. The aim of this work is to assess the performance of ED systems equipped with

121 profiled membranes of different geometry and quantify the effects on LCD and desalination
122 performance. Current–voltage characteristics were recorded under different operating conditions
123 mimicking both brackish water and seawater (limiting the analysis to the final stage of the process)
124 desalination conditions. Different profiling geometries were used, namely membranes with
125 Overlapped Crossed Filament profiles and with Pillar profiles, using conventional flat membranes for
126 comparison purposes. In all cases, the performance of the ED system was evaluated in terms of current
127 efficiency (η), LCD, and energy consumption.

128 **2 Experimental**

129 The present experimental campaign consisted of single-pass ED tests with lab-scale stacks equipped
130 either with profiled membranes or with conventional “flat” membranes and spacers. In particular,
131 current–voltage (i – V) curves were recorded in order to characterize the various ED stacks under
132 different operating conditions (inlet concentrations, fluid velocity and relative arrangement of the
133 profiles with respect to the direction of the electric current) mimicking seawater or brackish water
134 desalination with artificial NaCl solutions. At each applied current, the data collected were voltage
135 and outlet concentrations. The limiting current density was identified from the i – V curve. Current
136 efficiency and specific energy consumption were calculated.

137 **2.1 Materials and set-up**

138 The experimental campaign was carried out with a lab-scale ED stack (REDstack BV, The
139 Netherlands) composed of 10 cell pairs with active area of 100 cm² and characterized by cross-flow
140 layout of diluate and concentrate solutions. Fujifilm Type-10 CEM/AEM (Fujifilm Manufacturing
141 Europe BV, The Netherlands) were used for all the tests, and the main properties are reported in Table
142 1. Two types of profiled membranes were used: Overlapped Crossed Filaments (OCF) and Pillars.
143 Our research group studied similar geometries by numerical models ([65–68] for OCF profiles and
144 [57,69] for pillar profiles). Membrane profiles were prepared by the manufacturer by adding ion

145 conductive cross-linked resin on existing base membranes by a screen printing process. Profiles were
 146 built on one membrane side only, thus the resulting profiled membranes were asymmetrical.

147 Table 1. Properties of the Fujifilm Type 10 ion-exchange membranes used in this study. “n.p.” means “not provided”.

		Permselectivity ^a [%]	Water permeability [ml/(m ² h bar)]	Salt diffusivity [m ² /s]	IEC [meq/g]	Areal resistance ^b [Ω cm ²]	Thickness (dry) [μm]	Thickness (wet) [μm]	Profile thickness (wet) [μm]
Flat	AEM	97	6.29	4·10 ⁻¹²	2.85	1.77	120	130	-
	CEM	98	7.79	4·10 ⁻¹²	2.9	1.89	120	130	-
OCF 270^c	AEM	95.1	7.63	2.7·10 ⁻¹²	2.85	2.36	120	130	135
	CEM	99.5	5.26	2.7·10 ⁻¹²	n.p.	3.21	120	130	135
OCF 150^c	AEM	94.7	5.65	2·10 ⁻¹²	n.p.	2.07	120	130	75
	CEM	99.3	5.49	2·10 ⁻¹²	n.p.	2.8	120	130	75
Pillar 155^c	AEM	94.3	6.11	4.3·10 ⁻¹²	n.p.	1.89	120	130	155
	CEM	99	6.99	4.3·10 ⁻¹²	n.p.	2.48	120	130	155

148 ^a Determined from measurements of membrane potential with 0.05 M and 0.5 M KCl solutions at 25 °C.

149 ^b Measured in 2 M NaCl solution at 25 °C.

150 ^c The number identifies the nominal channel thickness (in μm), i.e. the pillar thickness for the Pillar-profiled membranes,
 151 and twice the profile thickness for OCF-profiled membranes.

152

153 The OCF-profiled membranes provide to the channel a geometry similar to that of non-woven spacer-
 154 filled channels. The OCF profiles were composed of continuous filaments with half-elliptic cross-
 155 section with major axis of 1 mm and thickness, representing the semi-minor axis, of either 135 or 75
 156 μm. The distance between two consecutive filaments was 1 mm. CEMs and AEMs were arranged in
 157 the stack with their profiles facing each other in the same channel and crossing at 90° (Figure 1a).
 158 The other channel of the cell pair was created by a net spacer. The thickness of the profile-filled

channel was thus twice the profile height (i.e., either 270 or 150 μm). Both OCF-profiled membranes (of either 135 or 75 μm profile thickness) had the same open area, represented by the free (i.e., non-profiled) fraction of the membrane area, of $\sim 50\%$. The profile-filled channel had a porosity of $\sim 61\%$. The main flow was directed at 45° of either filament. Between two adjacent OCF-profiled membranes, a gasket was interposed to seal the lateral regions of the profile-filled channel. It also included a piece of net spacer at the inlet/outlet regions close to the manifolds. Therefore, it confined the solution within the lateral sides of the channel and separated the membranes in the inlet/outlet regions.

The other channel of the cell pair, comprised between the flat sides of two adjacent OCF profiled membranes, was equipped with a woven spacer with integrated gasket. The spacer thickness was equal, or at least similar, with respect to that of the profile-filled channel, namely 270 or 155 μm . The spacers had a pitch-to-height ratio of 2, a porosity of $\sim 75\%$ and an open area of $\sim 50\%$. Therefore, the stack equipped with OCF-profiled membranes was actually hybrid, having one channel filled by membrane profiles and one channel filled by a net spacer.

The pillar-profiled membranes were characterized by a simpler geometrical configuration. The pillar profiles were semi-ellipsoidal ridges that can be approximated by parallelepipeds with square base with 1 mm side and thickness of 155 μm , placed on one side of the membrane (Figure 1b). The pillar profiles were arranged in a square lattice with $\sqrt{2}$ mm side (distance between the centres). The open area was $\sim 50\%$, as well as the volume channel porosity. The direction of the main flow was parallel to the diagonal of the profiles and of the lattice. Note that the tested pillar-profiled membranes were characterized by a reduction of active area. In a first approximation, the lateral active area of the pillar, calculated as $1 \times 0.155 \times 4 \text{ mm}^2$, was $\sim 60\%$ of the area that it subtracted from the adjacent membrane, equal to $1 \times 1 \text{ mm}^2$. Pillar-profiled membranes were arranged in the stack by putting in contact the flat side of each membrane with the profiled side of the adjacent membrane, thus the

channel thickness was determined by the profiles height ($\approx 155 \mu\text{m}$). Out of the active profiled area, a gasket was placed on each membrane.

For comparison purposes, the experimental campaign of the present study included tests with conventional ED units, using stacks equipped with flat membranes and woven spacers either 270 or 155 μm thick.

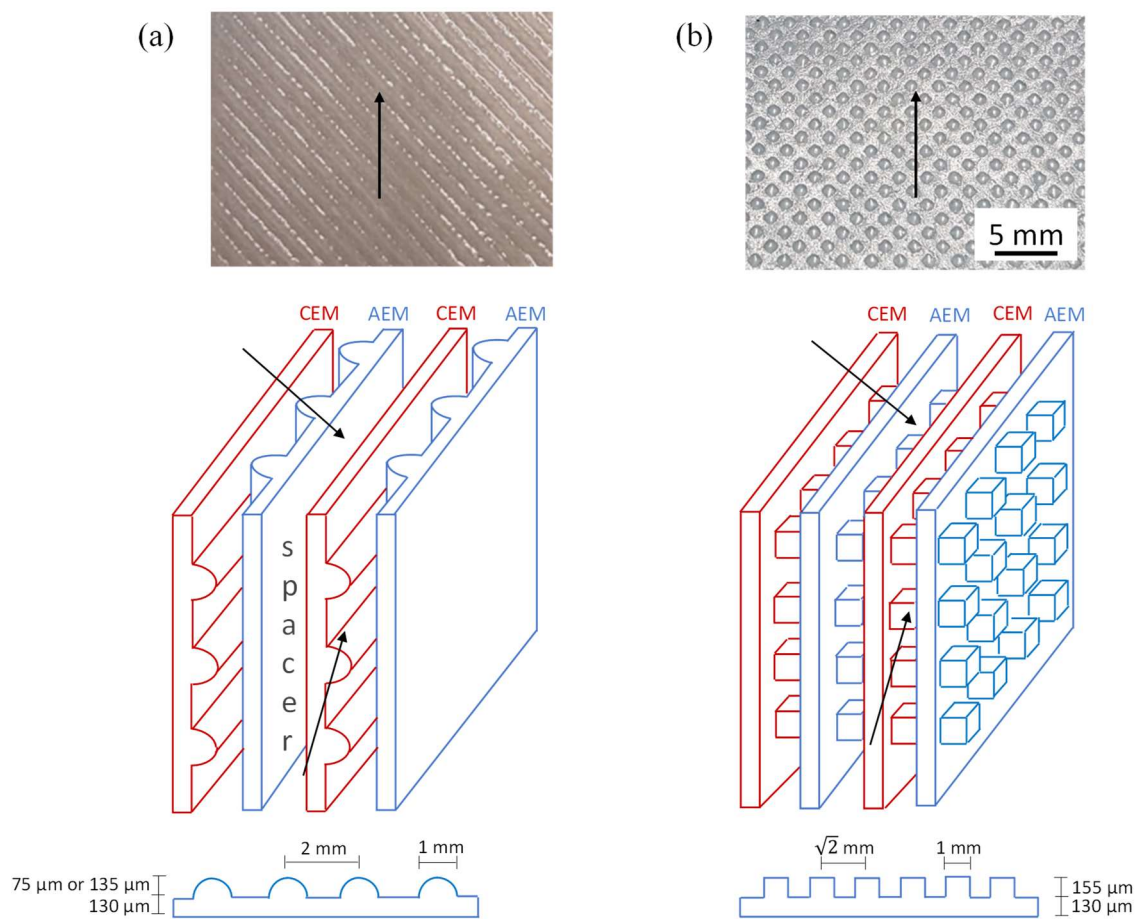
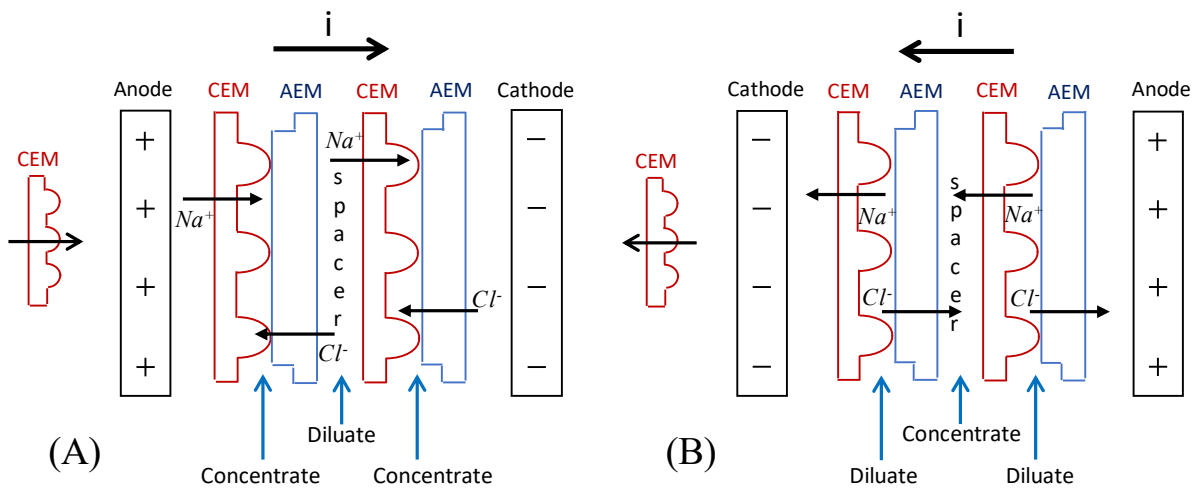


Figure 1. Picture of profiled membranes (top row), schematic representation of the stack assembly (middle row), and schematic cross-section of one profiled membrane (bottom row) with Overlapped Crossed Filament-profiled membranes (a) and Pillar-profiled membranes (b). Arrows indicate the flow direction (cross-flow layout). Note that the stack equipped with OCF-profiled membranes was arranged with profiles of adjacent IEMs facing each other at 90° in the same channel. The other channel of the cell pair was created by a net spacer.

196 The profiled membranes tested in this work are not symmetric, as the profiles were fabricated only
 197 on one side of the membrane. Therefore, the two channels of the cell pair were not identical. As a
 198 consequence, two different operating mode arisen, regarding the relative direction of the electric
 199 current and the position of the two solutions, which could lead to different behaviours and
 200 performances. Moreover, stacks with OCF-profiled membranes were in a “hybrid” configuration,
 201 with alternating profile-filled and spacer-filled channels. Therefore, the diluate could flow through
 202 the spacer-filled channel with the electric current going from the flat side to the profiled side of the
 203 CEM, or *vice versa* (Figure 2). In stacks equipped with pillar-profiled membranes, the compartments
 204 were created alternatively by profiles of either the AEM or the CEM. Therefore, the diluate could
 205 flow through the channel with AEM pillars, with the electric current going from the flat side to the
 206 profiled side of each IEM, or *vice versa* (Figure 3). The two different operating modes for the electric
 207 current direction in the stacks will be referred to as “A” and “B” hereafter. They were obtained by
 208 switching the current direction (i.e., the electrodes polarity) and, in the case of two inlet streams at
 209 different concentration, the diluate and concentrate channels.

210



211

212 Figure 2. Schematic cross-section illustrating the operating modes for OCF-profiled membrane stack: (A) electric current
 213 from flat to profiled side of CEM (i.e., diluate through the spacer-filled channels); (B) electric current from profiled to
 214 flat side of the CEM (i.e., diluate through the profile-filled channels).

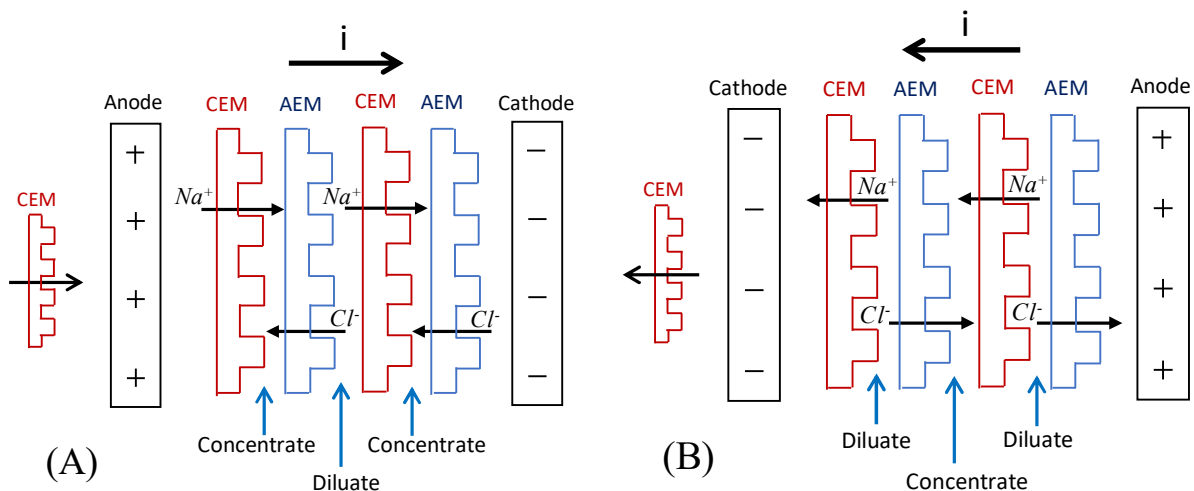


Figure 3. Schematic cross-section illustrating the operating modes for Pillar-profiled membrane stack: (A) electric current from flat to profiled side of each membrane (i.e., diluate through the AEM pillars); (B) electric current from profiled to flat side of each membrane (i.e., diluate through the CEM pillars). For clarity of the graphical representation, the pillar profiles of each membrane are shown detached from the adjacent membrane, though they are actually in contact when piled together within the stack.

Five stacks in total were tested, depending on the membranes used. By taking into account the two operating modes for the electric current in the case of stacks with profiled membranes, the labels indicated in the first and second row of Table 2 will be used hereafter. Table 2 indicates also the diluate and concentrate filling for each case.

Salt solutions (0.5, 1, 30 or 60 g/l) were prepared with demineralized water and NaCl (>99.5% purity, Saline di Volterra s.r.l., Italy or Regenit, Frisia Zout B.V., The Netherlands), and pumped as single-pass through the stack at different flow rates (see Table 3) with equal values for both streams. NaCl concentrations for concentrate and diluate were chosen to mimic solutions treated in the final stage of a multi-stage ED configuration or of a long stack for seawater desalination [18], as well as for brackish water desalination.

Table 2. Labels used to indicate the different stacks (with flat, or OCF-profiled or Pillar-profiled membranes, first row from the top) and the relative direction of the electric current (second row); diluate and concentrate compartment filling for each case (third and fourth row, respectively). The number in the label indicates the thickness of the channel (i.e., the distance between the flat parts of two adjacent membranes) in μm . “A” means that the electric current goes from the flat side to the profiled side of the CEM; “B” means that the electric current goes towards the opposite direction (i.e., from the flat side to the profiled side of the AEM).

Stack	Flat_270	Flat_155	OCF_270		OCF_150		Pillar_155	
Configuration			OCF_270_A	OCF_270_B	OCF_150_A	OCF_150_B	Pillar_155_A	Pillar_155_B
Diluate	spacer	spacer	spacer	profiles	spacer	profiles	AEM profiles	CEM profiles
Concentrate	spacer	spacer	profiles	spacer	profiles	spacer	CEM profiles	AEM profiles

239

Table 3. Operating conditions in terms of fluid velocity and inlet concentration of the salt solutions.

	Concentrate	Diluate
Inlet concentration [g/l NaCl]	0.5	0.5
	30	
	60	
	1	1
	30	
	60	
Superficial fluid velocity [cm/s]	0.25	
	0.5	
	1	

241

The stack electrodes consisted of titanium and iridium-MMO (mixed metal oxide) coated electrodes, fixed on a polymethylmethacrylate (PMMA) support. Figure 4 shows the overall experimental setup. The electrode rinse solution (ERS) was an aqueous solution of potassium hexacyanoferrates (II) trihydrate ($\geq 99\%$ purity, Honeywell FlukaTM, Germany), potassium hexacyanoferrates (III) ($\geq 99\%$ purity, Honeywell FlukaTM, China) and sodium chloride (purity as above) (0.3M $\text{K}_3\text{Fe}(\text{CN})_6$, 0.3M $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, 0.25M NaCl), pumped through the electrode compartments with a flow rate of 180 ml/min and recirculated in the ERS reservoir. CEMs were used as end-membranes, and one additional

CEM was used as shielding membrane on each electrode, thus avoiding the poisoning of AEMs by the ERS. Peristaltic pumps (Masterflex Cole-Palmer) were used to feed all the solutions. Pulsation dampers were installed at the inlet to minimize pulsation of the peristaltic pumps, ensuring a continuous flow entering the stack. The electric current was supplied to the stack by a DC power supply (Ivium Technologies, The Netherlands). Multimeters (Fluke 175) were used for the electric measurements. The electric conductivity of the solutions was measured by a portable conductivity-meter (WTW 314i). all experiments were conducted at room temperature ($\sim 20^\circ\text{C}$).

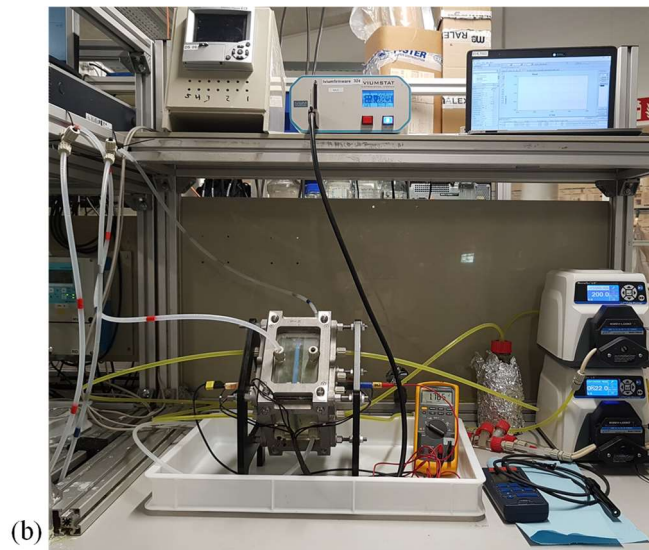
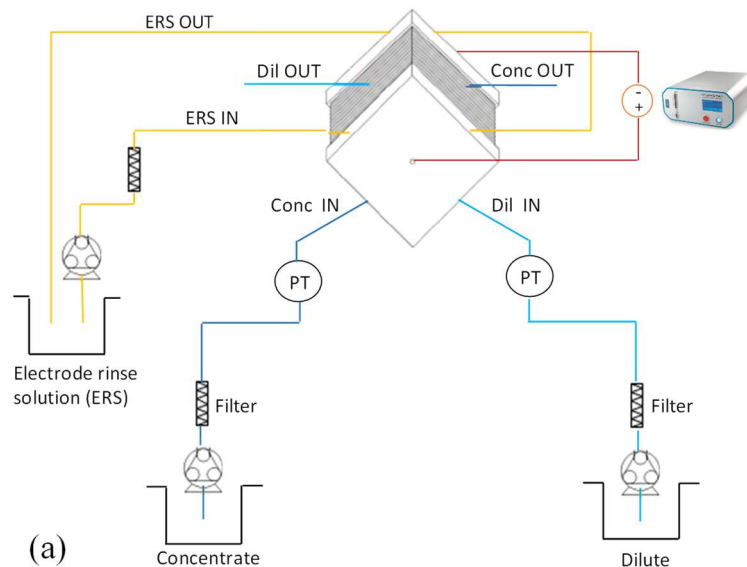


Figure 4. Schematic representation (a) and picture (b) of the experimental set-up.

260 2.2 Methods

261 After assembling the stack, hydraulic tests were conducted to detect and fix possible internal and
262 external leakages [70].

263 Current–voltage characteristics were built from chronopotentiometric measurements. After a short
264 period of open circuit, a constant current was applied and maintained for about ten times the residence
265 time of the solutions in the stack. The corresponding stationary voltage across the stack or its mean
266 value, in the presence of oscillation (limiting/overlimiting regime), was recorded. The applied current
267 was made to increase until it attained the limiting/overlimiting region, in order to collect information
268 both in underlimiting and in limiting conditions. Measurements were taken with two multimeters, one
269 as ammeter and the other as voltmeter, connected in series and in parallel, respectively, to the stack.
270 From the current–voltage curve, the limiting current density (LCD) was identified from the
271 intersection point between the straight line extrapolated from the first linear ohmic tract and the
272 tangent to the second region [71].

273 The current efficiency represents the fraction of current converted into useful salt flux, which is a
274 measure of how effectively the ion-exchange membranes lead to the selective passage of ions for a
275 given applied current [2]. By using the inlet-outlet mass balance of salt in the diluate channel, the
276 current efficiency (η) was calculated as:

$$277 \quad \eta = \frac{z F (Q_{dil,IN} C_{dil,IN} - Q_{dil,OUT} C_{dil,OUT})}{N_{CP} I M_w} \quad (2)$$

278 where $Q_{dil,IN}$ and $Q_{dil,OUT}$ are the total diluate flow rates at the inlet and outlet of the stack,
279 respectively (they were practically equal, thus indicating only small effects of osmosis and electro-
280 osmosis), $C_{dil,IN}$ and $C_{dil,OUT}$ are the mass concentrations of salt in the diluate at the inlet and the
281 outlet of the stack, respectively, N_{CP} is the number of cell pairs, I is the electric current, and M_w is
282 the molecular weight of the salt. For each value of applied current, the electrical conductivity was

283 measured for both outlets (diluate and concentrate), and the corresponding NaCl concentrations were
284 calculated by using an empirical correlation [72].

285 Finally, the specific energy consumption was calculated per unit volume of diluate product (SEC):

$$286 \quad SEC = \frac{V I}{Q_{dil,OUT}} \quad (3)$$

287 where V is the stack voltage.

288 The current density was calculated as the electric current divided by the projected area (i.e., 100 cm²).

289

290 **3 Results and Discussion**

291 The first part of the experimental campaign was focused on the influence of the operating mode (i.e.,
292 current direction, with respect to the membrane profiles), which can have a role in determining the
293 system performance because all the investigated profiled membranes are asymmetrical (i.e., single-
294 sided profiled) (section 3.1). Next, the best operating mode (in terms of highest LCD values) was
295 selected for the comparison tests among stacks with profiled membranes against conventional stacks
296 with flat membranes and spacers (section 3.2). In both sections, results are reported for a fluid velocity
297 of 1 cm/s and for two representative inlet concentration pairs, namely $C_{dil,IN} = C_{conc,IN} = 1$ g/l NaCl
298 (brackish water conditions) and $C_{dil,IN} = 0.5$ g/l, $C_{conc,IN} = 60$ g/l NaCl (i.e. mimicking the final stage
299 of a seawater desalination unit). Results at different feed conditions (inlet concentration and fluid
300 velocity) can be found in the Supplementary Data.

301

302 **3.1 Effect of current direction with respect to the profiles orientation**

303 Figure 5 reports typical results obtained with the OCF_270 profiled membranes. For both
304 concentration couples, the i - V curves (Figure 5a and b) exhibit a different behaviour between the two
305 current directions: after a first tract of overlapping (ohmic region), the two curves depart from each

other, and higher values of current density are reached for case “A” (electric current from the flat side to the OCF-profiled side of the CEM). Therefore, this configuration provided higher values of LCD. This behaviour may be partially explained by the enhanced mixing occurring in the woven spacer-filled channel [65], where the diluate flows (see Figure 2a). However, other reasons need to be claimed, due to the significantly different shape of the i - V curves. For example, note that case A and B are fundamentally different because of the different effective CEM (or AEM) area exposed to the diluate. Moreover, the i - V curve for the OCF_270_A resembles the typical trend found for homogeneous membranes (as the IEMs used in this work are), where the curve tends to a saturation (plateau) due to a gradual attainment of the LCD along the stack [73]. Instead, the OCF_270_B configuration exhibits a lower LCD and a longer inclined limiting/overlimiting region, thus resembling the typical trend found for heterogeneous membranes. This behaviour may be due to the presence of OCF profiles inside the diluate, which may act as geometrical heterogeneities (though macroscopic) causing a non-uniform local distribution of current density. In this case, the second region of the i - V curve can be already associated to an overlimiting state. The higher increase of i in the second region compared to the OCF_270_A case (i.e., the lower resistance) is a clue of the fact that other phenomena of ion transport are taking place, namely electroosmotic slip of the second kind (non-equilibrium electroconvection) and water splitting, which are favoured by non-uniform distributions of i . By testing similar two-side profiled membranes, a lower resistance in the second region compared to that of flat membranes and spacers was found in ref. [3], probably due to the membrane profiles present in the diluate.

The shape of the η - i curve (Figure 5c and d) is determined by the non-ideal behaviour of the membranes, and, specifically, by the unwanted transport of co-ions and water (via osmosis/electro-osmosis). All these fluxes increase with the current density, either because directly affected by the current (i.e., electro-osmosis) or indirectly (salt diffusion and osmosis, which are governed by increasing concentration gradient between concentrate and diluate). Therefore, there are two opposite

331 effects on the current efficiency as the electric current increases: on one side, the higher electro-
332 migration tends to increase η ; on the other side, higher undesired fluxes tend to reduce η . The
333 phenomenology is even more complex if we consider that the current density is not uniform, but is
334 higher close to the diluate inlet, where the stack resistance is lower. As the total current increases, the
335 current density tends to increase more in this zone. Therefore, a larger part of the cell pair is subject
336 to a high concentration gradient over the membranes. This behaviour makes co-ion diffusion and
337 osmosis further increase and, in some cases, may partially explain the reduction of η at high values
338 of electric current. However, this effect is negligible when, at the same time, (i) there is a large
339 concentration gradient between the inlet solutions and (ii) the diluate feed is at low concentration,
340 e.g., when 0.5-60 g/l solutions are used. In this case, in fact, the average concentration gradient would
341 increase only negligibly at higher current densities.

342 Therefore, the reduction of η at high values of i must be attributed, at least partially, to other reasons.
343 Some changes in the transport properties of IEMs may occur, leading to a loss of selectivity [74] and
344 to the prevalence of undesired transport mechanisms. As a consequence, the η - i curves exhibited
345 decreasing values after the maximum. These results support the hypothesis of a different response of
346 the profiled IEMs relative to the current direction (or, likewise, to profiles orientation during stack
347 assembly). In particular, higher values of current efficiency were obtained at high values of current
348 density in case A. Under this operating mode, η reached a maximum value over 99% when the
349 concentration gradient between the two solutions was low (1-1 g/l inlet concentrations, Figure 5c),
350 and of ~73% when the concentration gradient between the two solutions was high (0.5-60 g/l inlet
351 concentrations, Figure 5d). Instead, the maximum values of η were of ~98% and ~66% at 1-1 g/l and
352 0.5-60 g/l, respectively, for the worst direction of the electric current (case B).

353 Another possible reason behind (i) the reduction of η after the maximum and (ii) different behaviour
354 of the membranes depending on the electric current direction may be the occurrence of water splitting.
355 It can be favoured in case B, where “bipolar contacts” (i.e., the contact area between anion-exchange

and cation-exchange profiles/membranes) are in the diluate channel and a non-uniform distribution of current may occur. It is known that water splitting depends significantly on the catalytic activity of the functional groups and may occur even in the underlimiting region [75]. The ion-exchange matrix of the AEMs used in this work contains mainly quaternary ammonium bases, but also a small amount of secondary and tertiary amines [76], which have a catalytic activity [75]. Other phenomena reducing the current efficiency could be parasitic currents (or shunt currents) flowing via manifolds. However, given the low number of cell pairs (namely 10), we can reasonably assume that they were negligible in the present experiments [77].

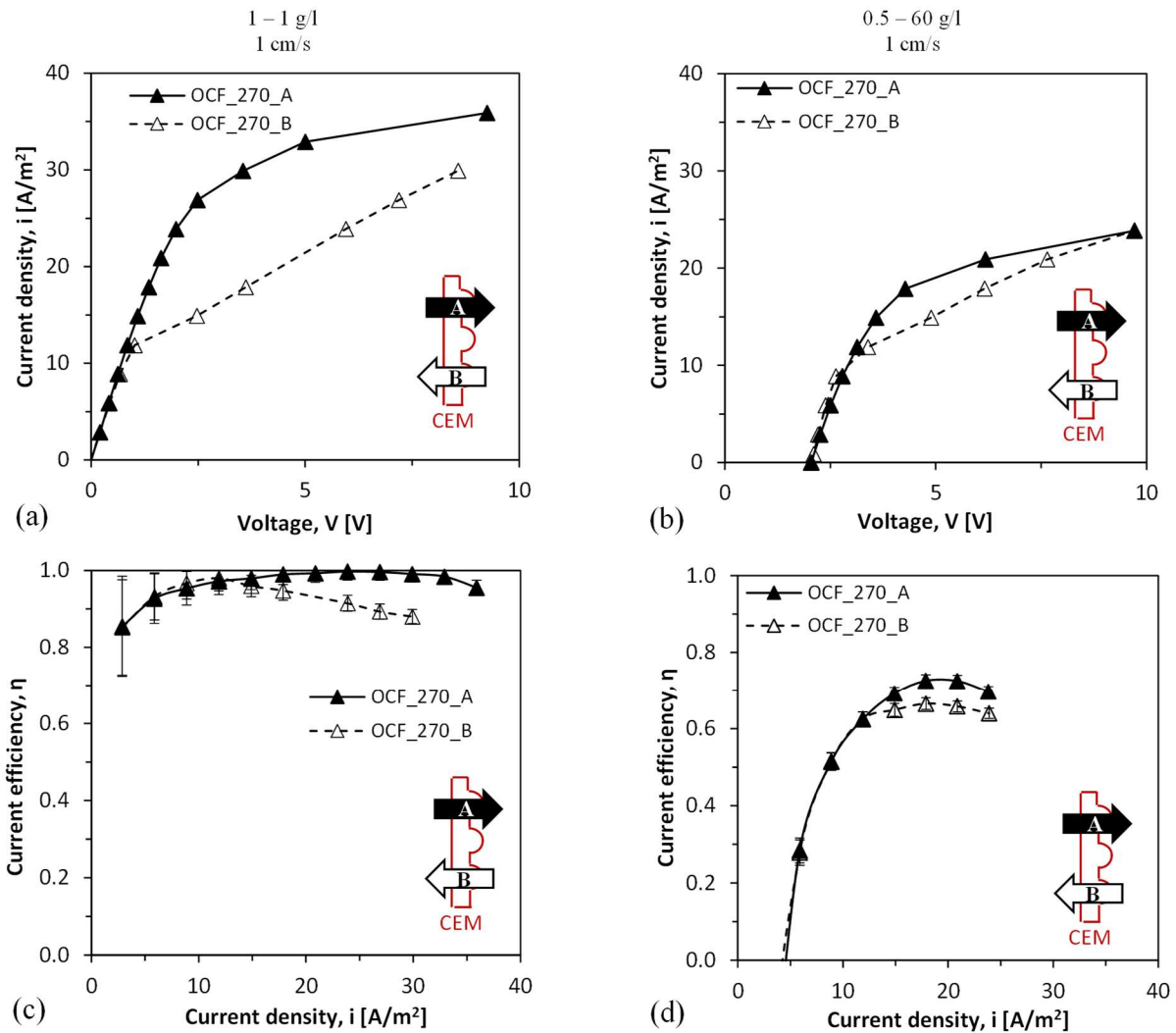


Figure 5. Current density–voltage curves (a,b) and current efficiency–current density curves (c,d) for the OCF_270 stack fed by inlet concentrations of $C_{dil,IN} = C_{conc,IN} = 1$ g/l (a,c) or $C_{dil,IN} = 0.5$ g/l and $C_{conc,IN} = 60$ g/l (b,d) at velocity of 1 cm/s. Two current operating modes are compared: case A (solid symbols) means current from flat side to profiled side of CEM;

368 Case B (hollow symbols) means current from profiled side to flat side of CEM. Error bars in the current efficiency (graph
369 c and d) were estimated by error propagation.

370

371 In the comparison between the different current directions (case A and B), similar results were
372 obtained in all the investigated operating conditions (in terms of inlet concentrations and velocity).
373 Considering the same stack of Figure 5 (OCF_270), Figure 6a and b show the effect of the inlet brine
374 concentration and of the fluid velocity (equal for both solutions), respectively, on the LCD. The
375 former parameter has been poorly studied so far, while the latter has been considered in many studies,
376 as well as the inlet diluate concentration. Interestingly, the LCD increases as the inlet brine
377 concentration increases (Figure 6a). This behaviour can be attributed to the higher interface
378 concentration in the diluate compartment resulting from higher values of back-diffusion and osmosis
379 [78]. A similar effect has been reported as a result of the higher diffusion permeability in thinner
380 membranes [79]. LCD was significantly higher for the OCF_270_A case (i.e., with profiles in the
381 diluate channel), with the largest relative difference found at equal inlet concentration (increase of
382 145% at 1-1 g/l) and decreasing by increasing the brine inlet concentration (increment of 128% at 1-
383 60 g/l) at 1 cm/s.

384 The LCD increases more markedly with the velocity (Figure 6b). The best current direction enhanced
385 more the LCD at higher velocities, being LCD more than doubled at 1 cm/s. By comparing the
386 rightmost points of Figure 6b and a, it can be observed that, as the inlet concentration of the diluate
387 increases from 0.5 g/l to 1.0 g/l, LCD values increase by ~50-80% (i.e., from 10 A/m² to 14.9 A/m²
388 for case B and from 19 A/m² to 34 A/m² for case A).

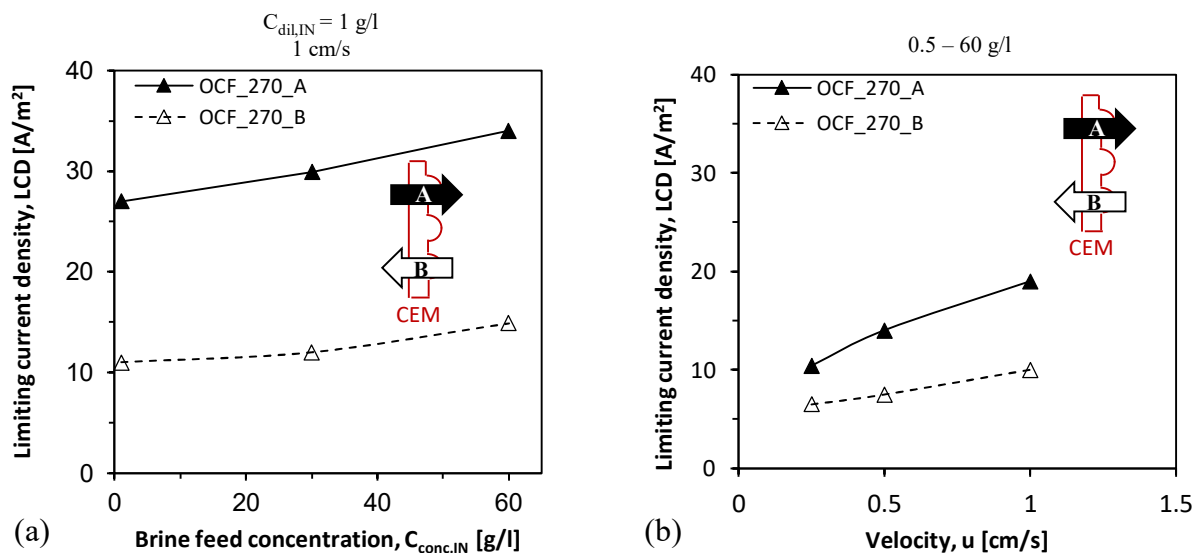


Figure 6. Limiting current density as a function of the concentrate inlet concentration for tests at $C_{dil,IN} = 1$ g/l and a velocity of 1 cm/s (a) and as a function of the velocity for tests at inlet concentrations of $C_{dil,IN} = 0.5$ g/l and $C_{conc,IN} = 60$ g/l (b) for the OCF_270 stack. Two current operating modes are compared: case A (solid symbols) means current from flat side to profiled side of CEM; Case B (hollow symbols) means current from profiled side to flat side of CEM.

Notably, the same behaviour in comparing case A and case B was found when testing the system with other types of profiled membranes (OCF_150 and Pillar_155, see the Supplementary Data). All the investigated profiled membranes showed better performance in the case “A”, in terms of higher values of LCD and current efficiency. In the Pillar_155 stack, the operating mode with the electric current flowing from the flat side to the profiled side of each membrane (case A) corresponds to having the diluate in the AEM profile-filled channel. In this case, the diluate compartment faces a larger AEM surface, which likely caused an increase in LCD as higher values are normally observed on AEMs than on CEMs. According to Eq. (1), the LCD is theoretically inversely proportional to the difference between the transport numbers of the counter-ion in membrane and solution. While the transport numbers of the counter-ions in the membranes are similar and close to 1, the transport numbers in solution are different ($t_{Na^+} \approx 0.4$ and $t_{Cl^-} \approx 0.6$). Therefore, the LCD on the AEM is about 1.5 times higher than that at the CEM [43].

3.2 Comparison between profiled and flat membrane stacks

Given the results analysed in section 3.1, the current direction from the flat side to the profiled side of the CEM (case A) was selected for all following experiments, which compare stacks equipped with profiled membranes against stacks equipped with flat membranes and net spacers.

3.2.1 Current-voltage curve, current efficiency and desalination performance

Figure 7 reports the current density–voltage curves for all stacks tested under different feed conditions (1-1 g/l and 0.5-60 g/l). All the i – V curves (Figure 7a and b) exhibit a first linear part, the ohmic region, followed by either a gradual reduction of slope towards a horizontal asymptote or an abrupt reduction of slope with an inclined limiting/overlimiting region. The first region does not exhibit appreciable differences among all stacks, meaning that they have practically the same ohmic resistance. Even stacks with similar profiled membranes or spacers, but with different channel thickness (OCF_270_A and OCF_150_A, and flat_270 and flat_155), exhibit the same resistance. This result can be explained by the higher average concentration of the diluate when the thickness was higher, due to the lower desalination achieved at a fixed velocity (Figure 7e and f). Therefore, the increase of resistance due to the higher thickness was counterbalanced by the increase of conductivity.

Instead, the limiting current behaviour was significantly different for the various stacks. The slope in the second region of the i – V curve (Figure 7a and b) decreased for stacks with OCF-profiled membranes or flat membranes. In the OCF_150_A case, a plateau was even approached. A linear second region was recorded for the Pillar_155_A case, probably because the presence of pillar profiles (of the AEM in case A) within the diluate implies the typical behaviour of systems with locally non-uniform current distribution. Clearly, these results had implications on the LCD. From the intersection point between the straight line extrapolated from the first region and the tangent to the second region [71], it is easy to recognise that the LCD with OCF-profiled membranes in case A is higher than with flat membranes for both values of channel thickness and for both couples of inlet

432 concentrations. It means that when the brine channel contains OCF membrane profiles and the dilute
433 channel is filled with the spacer, the LCD is higher than in the case with a spacer in both channels
434 (and flat membranes). This is an unexpected result, as the LCD is usually associated to phenomena
435 occurring in the diluate. The pillar-profiled membranes yielded the lowest values of LCD. More
436 details on the LCD are discussed in section 3.2.2.

437 Figure 7c and d report the current efficiency as a function of the current density for all stacks tested.
438 The two charts are significantly different. When the concentration gradient between the two
439 compartments was low (1-1 g/l inlet concentrations, Figure 7c) η was high (above 85% in most cases)
440 even at low values of i , as expected. Then, it slightly increased, exhibiting maximum values between
441 ~94% and ~99% and, finally, started decreasing roughly over the region of the i - V curve. The current
442 efficiency was higher in the OCF_270_A case than in the Flat_270 case, while the Flat_155 and
443 Pillar_155 cases yielded higher maximum values than the OCF_150_A case.

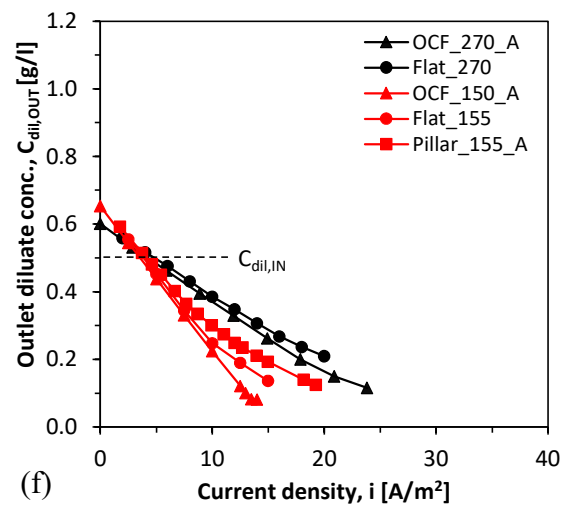
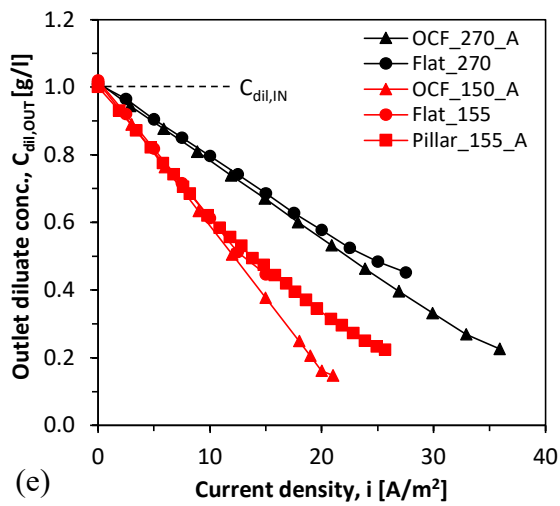
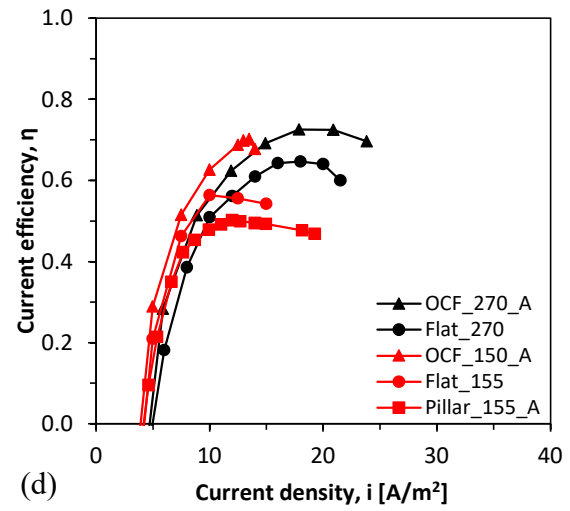
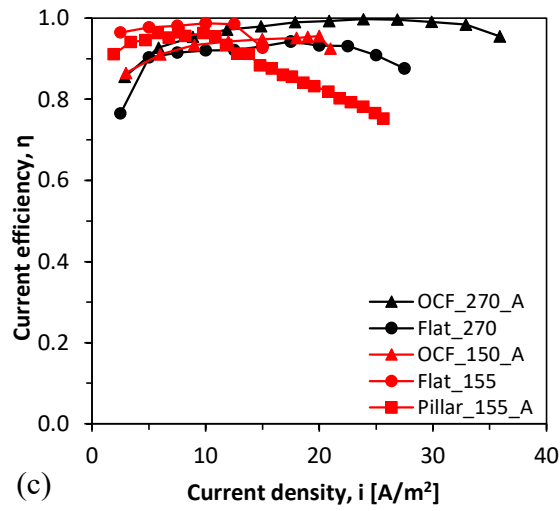
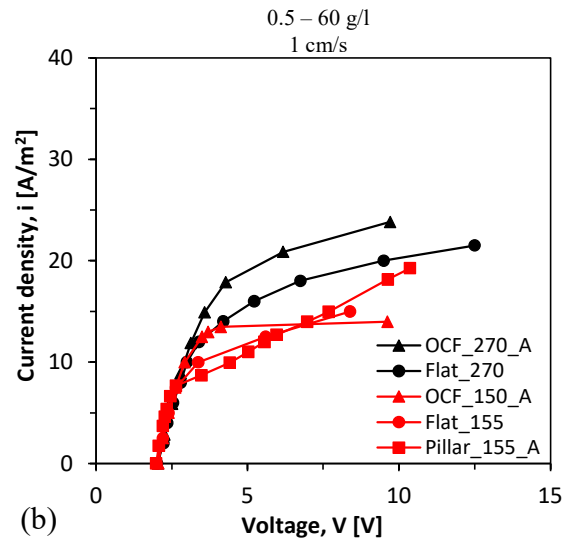
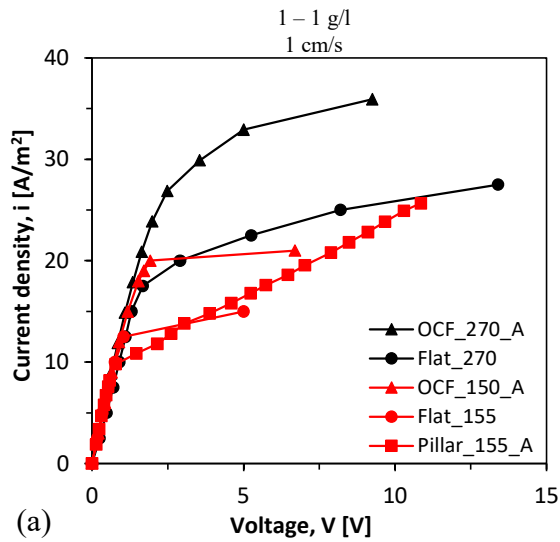
444 In the case of a high concentration gradient (0.5-60 g/l inlet concentrations, Figure 7d) the diffusive
445 flux of ions from concentrate to diluate is higher due to a higher driving force. Moreover, a lower
446 permselectivity of the membranes is expected with the 60 g/l brine [76], thus further increasing the
447 diffusive flux. At current densities below a critical value, the diffusive flux was even larger than the
448 electromigrative flux in the opposite direction, so that the concentration at the diluate outlet was
449 higher than that at the diluate inlet (Figure 7f), and the current efficiency was negative (Figure 7d)
450 according to its definition (Eq. 2). By increasing the current density, the electromigrative flux
451 overcomes the back-diffusive flux of ions, and the current efficiency rapidly increases with the current
452 density. The value of “critical current density” (i.e., the current leading to a net transport of ions equal
453 to zero and $\eta \approx 0$, [78]) was in the range of 3.5–5 A/m². Note that the values of the CCD were
454 practically coincident with those of the current density at which η was zero. In fact, the measured
455 change in flow rate from inlet to outlet was negligible. Given the small entity of (electro-)osmosis
456 compared to salt diffusion, the condition $C_{dil,OUT} = C_{dil,IN}$ corresponded to the condition $\eta = 0$. Then,

457 η increased up to maximum values between ~50% and ~70%, corresponding to the incipient limiting
 458 region for all stacks. Finally, η decreased in the rest of the i range tested. The current efficiency with
 459 OCF-profiled membranes was higher than with flat membranes or pillar-profiled membranes.

460 The current efficiency is strictly related to the outlet concentration, which is reported in Figure 7e and
 461 f for the diluate. The outlet concentration depends on the mass balance within the cell pair and is
 462 affected by unwanted transport phenomena. At 1-1 g/l inlet concentration, the desalination rate was
 463 higher than at 0.5-60 g/l due to the higher current efficiency. $C_{dil,OUT}$ followed a linear trend with i in
 464 the ohmic region of the i - V curve. Then, $C_{dil,OUT}$ reduced at a lower rate when the stack was operated
 465 in the limiting/overlimiting region where the current efficiency decreased. By comparing stacks with
 466 the same (or at least similar) channel thickness, the OCF_270_A test exhibited a higher desalination
 467 rate than the Flat_270 test, thanks to the higher values of η at any i . For the other three cases, the
 468 desalination rate was equal only in the under-limiting region at 1-1 g/l. Otherwise, the desalination
 469 rates were in descending order reflecting, obviously, that of the current efficiency (OCF_150_A >
 470 Flat_155 > Pillar_155_A). Of course, stacks with thicker channels yielded lower desalination rates
 471 than stacks with thinner channels, due to the higher flow rate (at fixed velocity).

472 As anticipated above, when the inlet concentrations differ from each other, there exists a non-null
 473 value of i that provides zero desalination ($C_{dil,OUT} = C_{dil,IN}$), referred to as “critical current density”
 474 (CCD) [78]. The knowledge of this parameter is important to be sure that the achievable LCD is
 475 sufficiently higher to guarantee a good flexibility to the unit. In the present experiments at 0.5-60 g/l
 476 (Figure 7f), the CCD was below ~5 A/m².

477 Results with other couples of inlet concentrations are reported in the Supplementary Data.



478

479

480

481

Figure 7. Current density–voltage curves (a,b), current efficiency–current density curves (c,d) and diluate outlet concentration–current density curves (e,f) for all the tested stacks fed by inlet concentrations of $C_{dil,IN} = C_{conc,IN} = 1$ g/l (a,c,e) or $C_{dil,IN} = 0.5$ g/l and $C_{conc,IN} = 60$ g/l (b,d,f) at velocity of 1 cm/s.

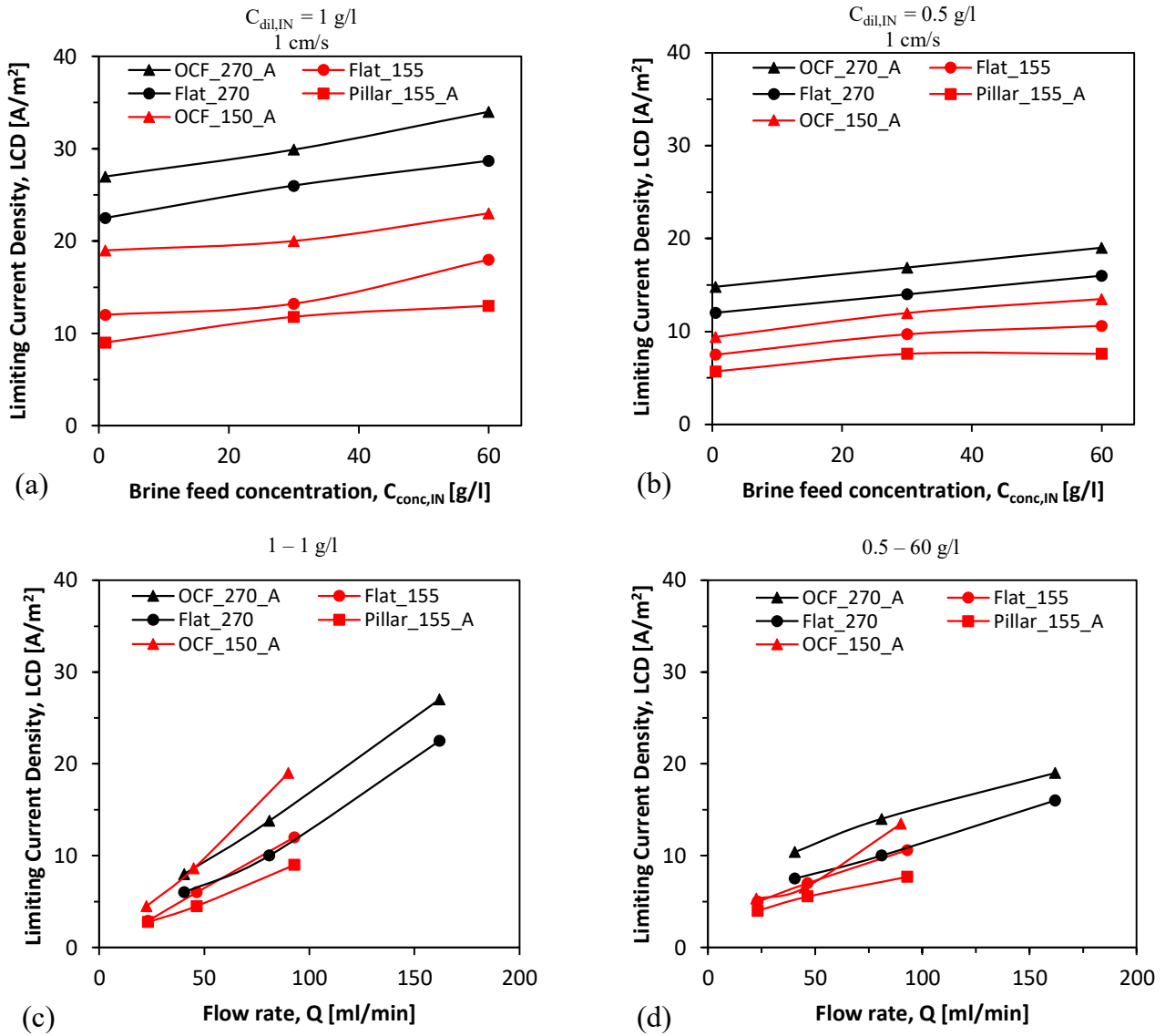
3.2.2 *Influence of operating conditions on limiting current density and energy consumption*

Figure 8 summarizes measurements of LCD collected under different experimental conditions and for all the different membranes tested. Overall, the LCD was comprised between ~ 2 and ~ 35 A/m². The inlet concentration of the brine had a weak positive effect on the LCD (back-diffusion), as shown in Figure 8a and b. By increasing the diluate inlet concentration from 0.5 g/l to 1.0 g/l (Figure 8b compared to Figure 8a), the LCD increases in all the investigated cases, as expected [27–29]. Figure 8a and b clearly show that OCF-profiled membranes enhance the LCD compared to flat membranes and pillar-profiled membranes.

Figure 8c and d report the LCD as a function of the flow rate for 1-1 g/l and 0.5-60 g/l, respectively. At 1-1 g/l, the LCD was roughly proportional to the flow rate, while at 0.5-60 g/l the effect of the flow rate was generally lower. A comparison among all stacks, which are basically divided in two groups depending on the channel thickness, is not straightforward, as the performance in terms of LCD depends significantly on the operating conditions. However, it is confirmed that OCF-profiled membranes outperformed flat membranes and pillar-profiled membranes in almost all cases. In particular, OCF_270_A and OCF_150_A cases were characterized by LCD values $\sim 20\%$ higher than the those of Flat_270 and Flat_155, respectively. The presence of the OCF profiles in substitution of the woven spacer in the concentrate compartment led to a different behaviour in the limiting region, which enhanced the LCD (as well as the current efficiency), as seen in section 3.2.1. Instead, pillar-profiled membranes exhibited the worst limiting behaviour and the lowest LCD under all experimental conditions. This configuration was probably affected by a poor mixing in the channel caused by stagnant regions [57,80] and by a reduced active area.

In some cases, e.g. Pillar_155_A, the LCD was so low that it was very close to the critical current density. Therefore, higher velocities may be recommended, as they would lead to higher values of the LCD without affecting the CCD. Otherwise, different feed conditions would be needed, if possible. On the other hand, the OCF_270_A configuration provided LCD values significantly higher

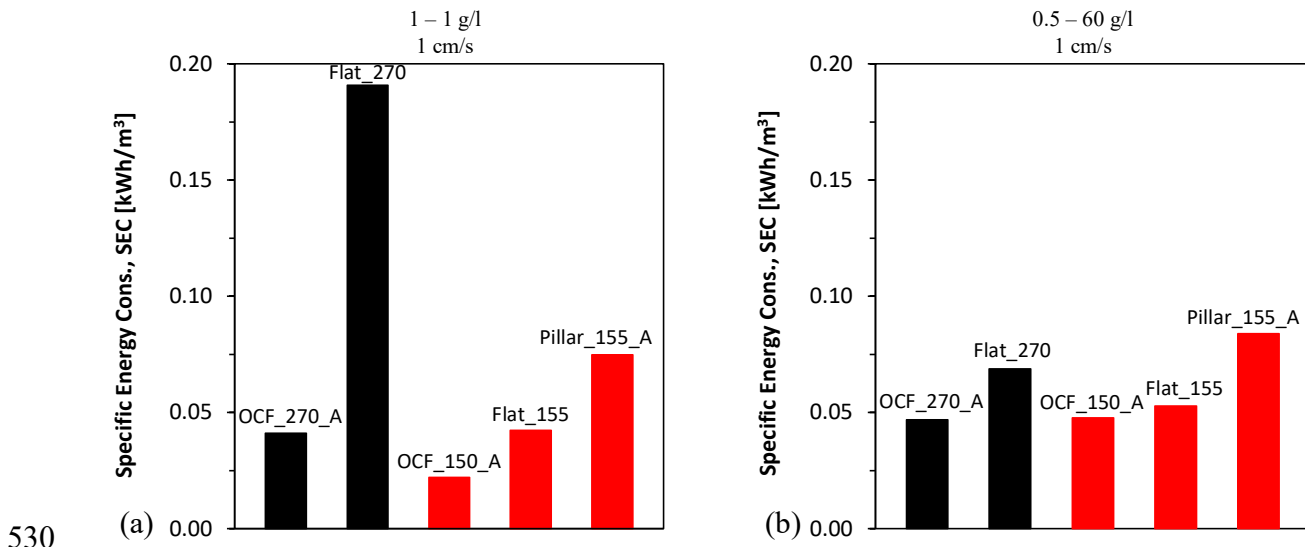
507 than the CCD, thus being more reliable and efficient for reaching the concentration target in the last
508 stages of seawater desalination.



509
510 Figure 8. Limiting current density as a function of the concentrate inlet concentration for tests at $C_{dil,IN} = 1$ g/l (a) or 0.5
511 g/l (b) at velocity of 1 cm/s; Limiting current density as a function of the flow rate for tests at inlet concentrations of $C_{dil,IN}$
512 $= C_{conc,IN} = 1$ g/l (c), and $C_{dil,IN} = 0.5$ g/l and $C_{conc,IN} = 60$ g/l (d).

513 Ohmic resistance, current efficiency and LCD may have a significant impact on the specific energy
514 consumption (SEC) of the different stacks. Figure 9 shows the SEC for the couples of inlet
515 concentrations of 1-1 g/l and 0.5-60 g/l fed at 1 cm/s to desalinate the diluate at an outlet concentration
516 of 0.5 or 0.3 g/l, respectively. By comparing stacks with the same (or very similar) channel thickness,

517 it can be observed that OCF-profiled membranes led to lower SECs than flat membranes, while Pillar-
 518 profiled membranes consumed the highest values of energy (OCF_270_A < Flat_270, and
 519 OCF_150_A < Flat_155 < Pillar_155_A). At 1-1 g/l (Figure 9a) and 0.5-60 g/l (Figure 9b) the
 520 reduction of the SEC was ~78% and ~32% from Flat_270 to OCF_270_A, respectively, while it was
 521 ~47% and ~10% from Flat_155 to OCF_150_A, respectively. Instead, the Pillar_155_A
 522 configuration increased the SECs by 70% on average compared to those of the Flat_155 case. This is
 523 in line with the current–voltage behaviour and the current efficiency observed in Figure 7. In fact, the
 524 conditions with higher SEC were those requiring a current density falling over the limiting region or,
 525 at least, in the last part of the first region of the i – V curve, where the stack resistance is high (see
 526 Figure 7). This is very evident for 270 μ m channels with 1-1 g/l inlet concentrations (Figure 9a, black
 527 histograms), for which the current density of ~23 A/m² required to obtain a diluate outlet
 528 concentration of 0.5 g/l (Figure 7e) was achieved by applying ~2 and 7 V for the cases OCF_270_A
 529 and Flat_270, respectively (Figure 7a).



531 Figure 9. Specific energy consumption for tests at inlet concentrations of $C_{dil,IN} = C_{conc,IN} = 1$ g/l (a) and $C_{dil,IN} = 0.5$ g/l
 532 and $C_{conc,IN} = 60$ g/l (b) to obtain a diluate outlet concentration of 0.5 g/l (in graph a) or 0.3 g/l (in graph b), respectively,
 533 at velocity of 1 cm/s.

534 4 Conclusions

535 The aim of this work has been to investigate the use of asymmetrically profiled membranes in ED for
536 brackish water and seawater desalination. The orientation of the electric current with respect to
537 membrane profiles should be carefully considered. The operation with the electric current directed
538 from the flat side to the profiled side of the CEM (case “A”) was preferable. For example, the
539 OCF_270_A case outperformed the alternative case of current direction (OCF_270_B) by exhibiting
540 (i) higher maximum η (e.g., ~73% against ~66% at 0.5-60 g/l inlet concentrations and 1 cm/s) and
541 (ii) roughly double LCDs under various operating conditions. The worse performance in the case
542 OCF_270_B can be explained by the detrimental effects associated to a non-uniform local current
543 distribution caused by the profiles in the diluate.

544 The OCF_A cases exhibited better performances than stacks with flat membranes. The maximum η
545 increased, for example, from ~55–65% for Flat_270 and Flat_155 to ~70–73% for OCF_270_A and
546 OCF_150_A at 0.5-60 g/l inlet concentrations. The LCD of stacks with OCF-profiled membranes
547 increased roughly by 20% under various operating conditions. Instead, the stack with Pillar-profiled
548 membranes, even when operated with the best current direction (Pillar_155_A case), yielded worse
549 performances compared to the Flat_155 stack, probably due to the detrimental effects associated to a
550 locally non-uniform current distribution in the diluate and to a poor mixing. Stacks with flat
551 membranes, which were assembled with woven spacers in all channels (e.g., Flat_270), achieved
552 performances somehow in between those of the hybrid stacks with OCF profiles and woven spacers
553 with one or the other direction of the electric current (e.g., OCF_270_A and OCF_270_B). The
554 enhancement of the LCD and η due to the presence of membrane profiles in the brine channel is an
555 unexpected and interesting result that deserves further study.

556 The specific energy consumption calculated for a diluate desalination of 0.5 g/l or 0.2 g/l for 1-1 g/l
557 or 0.5-60 g/l inlet concentrations, respectively, was reduced by OCF-profiled membranes by 10–78%
558 with respect to stacks with flat membranes, which required overlimiting currents. By resulting in

559 higher η and LCD, profiled membranes may reduce membrane area and capital costs. Moreover,
560 well-designed profiled membranes can reduce the overall desalination cost, thus prompting the
561 development of competitive systems in applications where ED has been too much expensive so far.
562 In particular, OCF-profiled membranes are very promising and deserve further studies.

563 Symmetrical (i.e., double-sided) profiled membranes should be characterized to provide a more
564 complete framework. However, their fabrication is still technically challenging, and further research
565 efforts are needed. Moreover, they would be of interest to ensure good performance also during
566 polarity switch for fouling removal in EDR operations. In this regard, the characterization of ED
567 stacks equipped with profiled membranes for the desalination of natural feedwater is still lacking.
568 Finally, the electrochemical characterization of the profiled membranes is recommended to provide
569 a thorough description of their behaviour at the origin of the ED performance.

570

571 **Acknowledgments**

572 This work was performed in the framework of the REvived water project (Low energy solutions for
573 drinking water production by a REvival of ElectroDialysis systems). This project has received
574 funding from the European Union's Horizon 2020 Research and Innovation program under Grant
575 Agreement no. 685579 (www.revivedwater.eu).

576 The authors are grateful to REDstack B.V. for supplying the ED stack and to Fujifilm Manufacturing
577 Europe B.V. for supplying all the membranes for this study.

578 The authors are also grateful to Dr. Mariagiorgia La Cerva and Ms. Serena Bellia for their precious
579 contribution in collecting experimental data and providing useful suggestions.

580 **List of abbreviations**

581 AEM Anion-exchange membrane

582 CCD Critical current density

583 CEM Cation-exchange membrane

584 ED Electro dialysis

585 IEM Ion-exchange membrane

586 LCD Limiting current density

587 OCF Overlapped crossed filament

588 SEC Specific energy consumption

589

590 **References**

- 591 [1] A. Campione, L. Gurreri, M. Ciofalo, G. Micale, A. Tamburini, A. Cipollina, Electrodialysis
592 for water desalination: A critical assessment of recent developments on process fundamentals,
593 models and applications, *Desalination*. 434 (2018) 121–160. doi:10.1016/j.desal.2017.12.044.
- 594 [2] J.R. Wilson, *Demineralization by electrodialysis*, Butterworths Scientific Publications,
595 London, 1960.
- 596 [3] H. Strathmann, Electrodialysis, a mature technology with a multitude of new applications,
597 *Desalination*. 264 (2010) 268–288. doi:10.1016/j.desal.2010.04.069.
- 598 [4] C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production
599 of organic acids: State-of-the-art and recent developments, *J. Memb. Sci.* 288 (2007) 1–12.
600 doi:10.1016/j.memsci.2006.11.026.
- 601 [5] T. Xu, C. Huang, Electrodialysis-Based separation technologies: A critical review, *AIChE J.*
602 54 (2008) 3147–3159. doi:10.1002/aic.11643.
- 603 [6] J. Ran, L. Wu, Y. He, Z. Yang, Y. Wang, C. Jiang, L. Ge, E. Bakangura, T. Xu, Ion exchange

- 604 membranes: New developments and applications, *J. Memb. Sci.* 522 (2017) 267–291.
 605 doi:10.1016/j.memsci.2016.09.033.
- 606 [7] L. Gurreri, A. Tamburini, A. Cipollina, G. Micale, Electrodialysis applications in wastewater
 607 treatments for environmental protection and resources recovery: a systematic review on
 608 progress and perspectives, *Membranes (Basel)*. 10 (2020) 1–82.
 609 doi:10.3390/membranes10070146.
- 610 [8] International Desalination Association (IDA), *Desalination Yearbook 2016-2017*, 2017.
- 611 [9] E. Jones, M. Qadir, M.T.H. van Vliet, V. Smakhtin, S. mu Kang, The state of desalination and
 612 brine production: A global outlook, *Sci. Total Environ.* 657 (2019) 1343–1356.
 613 doi:10.1016/j.scitotenv.2018.12.076.
- 614 [10] A. Al-Karaghoul, L.L. Kazmerski, Energy consumption and water production cost of
 615 conventional and renewable-energy-powered desalination processes, *Renew. Sustain. Energy*
 616 *Rev.* 24 (2013) 343–356. doi:10.1016/j.rser.2012.12.064.
- 617 [11] REvived water, (n.d.). <https://www.revivedwater.eu/>.
- 618 [12] R.K. McGovern, S.M. Zubair, J.H. Lienhard V, The cost effectiveness of electrodialysis for
 619 diverse salinity applications, *Desalination*. 348 (2014) 57–65.
 620 doi:10.1016/j.desal.2014.06.010.
- 621 [13] K.M. Chehayeb, K.G. Nayar, J.H. Lienhard, On the merits of using multi-stage and
 622 counterflow electrodialysis for reduced energy consumption, *Desalination*. 439 (2018) 1–16.
 623 doi:10.1016/j.desal.2018.03.026.
- 624 [14] M. La Cerva, L. Gurreri, A. Cipollina, A. Tamburini, M. Ciofalo, G. Micale, Modelling and
 625 cost analysis of hybrid systems for seawater desalination: Electromembrane pre-treatments for
 626 Reverse Osmosis, *Desalination*. 467 (2019) 175–195. doi:10.1016/j.desal.2019.06.010.
- 627 [15] A. Campione, A. Cipollina, I.D.L. Bogle, L. Gurreri, A. Tamburini, M. Tedesco, G. Micale, A

- 628 hierarchical model for novel schemes of electrodialysis desalination, *Desalination*. 465 (2019)
 629 79–93. doi:10.1016/J.DESAL.2019.04.020.
- 630 [16] M.M. Generous, N.A.A. Qasem, S.M. Zubair, The significance of modeling electrodialysis
 631 desalination using multi-component saline water, *Desalination*. (2020) 114347.
 632 doi:10.1016/j.desal.2020.114347.
- 633 [17] A.H. Galama, M. Saakes, H. Bruning, H.H.M. Rijnaarts, J.W. Post, Seawater predesalination
 634 with electrodialysis, *Desalination*. 342 (2014) 61–69. doi:10.1016/j.desal.2013.07.012.
- 635 [18] G.J. Doornbusch, M. Tedesco, J.W. Post, Z. Borneman, K. Nijmeijer, Experimental
 636 investigation of multistage electrodialysis for seawater desalination, *Desalination*. 464 (2019)
 637 105–114. doi:10.1016/j.desal.2019.04.025.
- 638 [19] G.J. Doornbusch, M. Bel, M. Tedesco, J.W. Post, Z. Borneman, K. Nijmeijer, Effect of
 639 membrane area and membrane properties in multistage electrodialysis on seawater desalination
 640 performance, *J. Memb. Sci.* 611 (2020) 118303. doi:10.1016/j.memsci.2020.118303.
- 641 [20] S. Porada, W.J. van Egmond, J.W. Post, M. Saakes, H.V.M. Hamelers, Tailoring ion exchange
 642 membranes to enable low osmotic water transport and energy efficient electrodialysis, *J.*
 643 *Memb. Sci.* 552 (2018) 22–30. doi:10.1016/j.memsci.2018.01.050.
- 644 [21] J. Kamcev, C.M. Doherty, K.P. Lopez, A.J. Hill, D.R. Paul, B.D. Freeman, Effect of fixed
 645 charge group concentration on salt permeability and diffusion coefficients in ion exchange
 646 membranes, *J. Memb. Sci.* 566 (2018) 307–316. doi:10.1016/j.memsci.2018.08.053.
- 647 [22] J. Kamcev, D.R. Paul, G.S. Manning, B.D. Freeman, Ion Diffusion Coefficients in Ion
 648 Exchange Membranes: Significance of Counterion Condensation, *Macromolecules*. 51 (2018)
 649 5519–5529. doi:10.1021/acs.macromol.8b00645.
- 650 [23] M. Ciofalo, M. Di Liberto, L. Gurreri, M. La Cerva, L. Scelsi, G. Micale, Mass transfer in
 651 ducts with transpiring walls, *Int. J. Heat Mass Transf.* 132 (2019) 1074–1086.

doi:10.1016/J.IJHEATMASTRANSFER.2018.12.059.

- [24] D. Butylskii, I. Moroz, K. Tsygurina, S. Mareev, Effect of Surface Inhomogeneity of Ion-Exchange Membranes on the Mass Transfer Efficiency in Pulsed Electric Field Modes, *Membranes (Basel)*. 10 (2020) 40. doi:10.3390/membranes10030040.
- [25] F. Sheng, N.U. Afsar, Y. Zhu, L. Ge, T. Xu, PVA-based mixed matrix membranes comprising ZSM-5 for cations separation, *Membranes (Basel)*. 10 (2020) 1–16. doi:10.3390/membranes10060114.
- [26] W.J. Koros, Y.H. Ma, T. Shimidzu, Terminology for membranes and membrane processes (IUPAC Recommendations 1996), *Pure Appl. Chem.* 68 (1996) 1479–1489. doi:10.1351/pac199668071479.
- [27] T.L. Hill, G. Scatchard, B.A. Pethica, I.J. Straub, R. Schlögl, G. Manecke, R. Schlögl, M. Nagasawa, I. Kagawa, P. Meares, K. Sollner, F.L. Tye, A. Despiá, G.J. Hills, F. Helfferich, J.E. Salmon, R.J.P. Williams, A.M. Peers, F. Bergsma, A.J. Staverman, N. Krishnaswamy, F. Runge, F. Wolf, E. Glueckauf, D. Reichenberg, R. Neihof, R.D. Keynes, A.R. Ubbelohde, R.M. Barrer, General discussion, *Discuss. Faraday Soc.* 21 (1956) 117–140. doi:10.1039/DF9562100117.
- [28] F. Helfferich, *Ion exchange*, McGraw-Hill, New York, 1962.
- [29] V.G. Levich, *Physicochemical Hydrodynamics*, Prentice-Hall, Englewood Cliffs, N.J., 1962.
- [30] V. V. Nikonenko, S.A. Mareev, N.D. Pis'menskaya, A.M. Uzdenova, A. V. Kovalenko, M.K. Urtenov, G. Pourcelly, Effect of electroconvection and its use in intensifying the mass transfer in electrodialysis (Review), *Russ. J. Electrochem.* 53 (2017) 1122–1144. doi:10.1134/S1023193517090099.
- [31] V. V. Nikonenko, N.D. Pismenskaya, E.I. Belova, P. Sistat, P. Huguet, G. Pourcelly, C. Larchet, Intensive current transfer in membrane systems: Modelling, mechanisms and

- 676 application in electrodialysis, *Adv. Colloid Interface Sci.* 160 (2010) 101–123.
 677 doi:10.1016/j.cis.2010.08.001.
- 678 [32] H.J. Lee, H. Strathmann, S.H. Moon, Determination of the limiting current density in
 679 electrodialysis desalination as an empirical function of linear velocity, *Desalination*. 190
 680 (2006) 43–50. doi:10.1016/j.desal.2005.08.004.
- 681 [33] Y. Sano, X. Bai, S. Amagai, A. Nakayama, Effect of a porous spacer on the limiting current
 682 density in an electro-dialysis desalination, *Desalination*. 444 (2018) 151–161.
 683 doi:10.1016/j.desal.2018.01.034.
- 684 [34] N.C. Wright, S.R. Shah, S.E. Amrose, A.G. Winter, A robust model of brackish water
 685 electrodialysis desalination with experimental comparison at different size scales,
 686 *Desalination*. 443 (2018) 27–43. doi:10.1016/j.desal.2018.04.018.
- 687 [35] C.C.N. Kunrath, D.C. Patrocínio, M.A. Siqueira Rodrigues, T. Benvenuti, F.D.R. Amado,
 688 Electrodialysis reversal as an alternative treatment for producing drinking water from brackish
 689 river water: A case study in the dry season, northeastern Brazil, *J. Environ. Chem. Eng.* 8
 690 (2020) 103719. doi:10.1016/j.jece.2020.103719.
- 691 [36] R. Simons, Water splitting in ion exchange membranes, *Electrochim. Acta*. 30 (1985) 275–
 692 282. doi:10.1016/0013-4686(85)80184-5.
- 693 [37] V. Nikonenko, M. Urtenov, S. Mareev, G. Pourcelly, Mathematical modeling of the effect of
 694 water splitting on ion transfer in the depleted diffusion layer near an ion-exchange membrane,
 695 *Membranes (Basel)*. 10 (2020). doi:10.3390/membranes10020022.
- 696 [38] V. V. Nikonenko, A. V. Kovalenko, M.K. Urtenov, N.D. Pismenskaya, J. Han, P. Sistat, G.
 697 Pourcelly, Desalination at overlimiting currents: State-of-the-art and perspectives,
 698 *Desalination*. 342 (2014) 85–106. doi:10.1016/j.desal.2014.01.008.
- 699 [39] A. Uzdenova, M. Urtenov, Potentiodynamic and galvanodynamic regimes of mass transfer in

- 700 flow-through electrodialysis membrane systems: Numerical simulation of electroconvection
701 and current-voltage curve, *Membranes (Basel)*. 10 (2020). doi:10.3390/membranes10030049.
- 702 [40] V.I. Zabolotsky, V. V. Nikonenko, N.D. Pismenskaya, E. V. Laktionov, M.K. Urtenov, H.
703 Strathmann, M. Wessling, G.H. Koops, Coupled transport phenomena in overlimiting current
704 electrodialysis, *Sep. Purif. Technol.* 14 (1998) 255–267. doi:10.1016/S1383-5866(98)00080-
705 X.
- 706 [41] J.J. Krol, M. Wessling, H. Strathmann, Chronopotentiometry and overlimiting ion transport
707 through monopolar ion exchange membranes, *J. Memb. Sci.* 162 (1999) 155–164.
708 doi:10.1016/S0376-7388(99)00134-9.
- 709 [42] B. Zaltzman, I. Rubinstein, Electro-osmotic slip and electroconvective instability, *J. Fluid*
710 *Mech.* 579 (2007) 173–226. doi:10.1017/S0022112007004880.
- 711 [43] R. Kwak, G. Guan, W.K. Peng, J. Han, Microscale electrodialysis: Concentration profiling and
712 vortex visualization, *Desalination*. 308 (2013) 138–146. doi:10.1016/j.desal.2012.07.017.
- 713 [44] I. Rubinstein, Electroconvection at an electrically inhomogeneous permselective interface,
714 *Phys. Fluids A*. 3 (1991) 2301–2309. doi:10.1063/1.857869.
- 715 [45] J. Balster, M.H. Yildirim, D.F. Stamatialis, R. Ibanez, R.G.H. Lammertink, V. Jordan, M.
716 Wessling, Morphology and microtopology of cation-exchange polymers and the origin of the
717 overlimiting current, *J. Phys. Chem. B*. 111 (2007) 2152–2165. doi:10.1021/jp068474t.
- 718 [46] V. Nikonenko, A. Nebavsky, S. Mareev, A. Kovalenko, M. Urtenov, G. Pourcelly, Modelling
719 of Ion Transport in Electromembrane Systems: Impacts of Membrane Bulk and Surface
720 Heterogeneity, *Appl. Sci.* 9 (2018) 25. doi:10.3390/app9010025.
- 721 [47] V. V. Gil, M.A. Andreeva, L. Jansezian, J. Han, N.D. Pismenskaya, V. V. Nikonenko, C.
722 Larchet, L. Dammak, Impact of heterogeneous cation-exchange membrane surface
723 modification on chronopotentiometric and current–voltage characteristics in NaCl, CaCl₂ and

- 724 MgCl₂ solutions, *Electrochim. Acta.* 281 (2018) 472–485.
 725 doi:10.1016/j.electacta.2018.05.195.
- 726 [48] S. Zyryanova, S. Mareev, V. Gil, E. Korzhova, N. Pismenskaya, V. Sarapulova, O. Rybalkina,
 727 E. Boyko, C. Larchet, L. Dammak, V. Nikonenko, How electrical heterogeneity parameters of
 728 ion-exchange membrane surface affect the mass transfer and water splitting rate in
 729 electrodialysis, *Int. J. Mol. Sci.* 21 (2020) 973. doi:10.3390/ijms21030973.
- 730 [49] K.A. Nebavskaya, V. V. Sarapulova, K.G. Sabbatovskiy, V.D. Sobolev, N.D. Pismenskaya, P.
 731 Sistat, M. Cretin, V. V. Nikonenko, Impact of ion exchange membrane surface charge and
 732 hydrophobicity on electroconvection at underlimiting and overlimiting currents, *J. Memb. Sci.*
 733 523 (2017) 36–44. doi:10.1016/j.memsci.2016.09.038.
- 734 [50] V. Titorova, K. Sabbatovskiy, V. Sarapulova, E. Kirichenko, V. Sobolev, K. Kirichenko,
 735 Characterization of MK-40 membrane modified by layers of cation exchange and anion
 736 exchange polyelectrolytes, *Membranes* (Basel). 10 (2020) 20.
 737 doi:10.3390/membranes10020020.
- 738 [51] C. Larchet, V.I. Zabolotsky, N. Pismenskaya, V. V. Nikonenko, A. Tskhay, K. Tastanov, G.
 739 Pourcelly, Comparison of different ED stack conceptions when applied for drinking water
 740 production from brackish waters, *Desalination.* 222 (2008) 489–496.
 741 doi:10.1016/j.desal.2007.02.067.
- 742 [52] S. Pawlowski, J.G. Crespo, S. Velizarov, Profiled ion exchange membranes: A comprehensible
 743 review, *Int. J. Mol. Sci.* 20 (2019) 165. doi:10.3390/ijms20010165.
- 744 [53] J. Balster, D.F. Stamatialis, M. Wessling, Membrane with integrated spacer, *J. Memb. Sci.* 360
 745 (2010) 185–189. doi:10.1016/j.memsci.2010.05.011.
- 746 [54] Y. Zhao, H. Wang, C. Jiang, L. Wu, T. Xu, Electrodialysis with notched ion exchange
 747 membranes: Experimental investigations and computational fluid dynamics simulations, *Sep.*

- Purif. Technol. 130 (2014) 102–111. doi:10.1016/j.seppur.2014.04.010.
- [55] S. Melnikov, S. Loza, M. Sharafan, V. Zabolotskiy, Electrodialysis treatment of secondary steam condensate obtained during production of ammonium nitrate. Technical and economic analysis, Sep. Purif. Technol. 157 (2016) 179–191. doi:10.1016/j.seppur.2015.11.025.
- [56] D.A. Vermaas, M. Saakes, K. Nijmeijer, Power generation using profiled membranes in reverse electrodialysis, J. Memb. Sci. 385–386 (2011) 234–242. doi:10.1016/j.memsci.2011.09.043.
- [57] L. Gurreri, M. Ciofalo, A. Cipollina, A. Tamburini, W. Van Baak, G. Micale, CFD modelling of profiled-membrane channels for reverse electrodialysis, Desalin. Water Treat. 55 (2015) 3404–3423. doi:10.1080/19443994.2014.940651.
- [58] J.G.D. Tadimeti, V. Kurian, A. Chandra, S. Chattopadhyay, Corrugated membrane surfaces for effective ion transport in electrodialysis, J. Memb. Sci. 499 (2016) 418–428. doi:10.1016/j.memsci.2015.11.001.
- [59] L. Gurreri, G. Battaglia, A. Tamburini, A. Cipollina, G. Micale, M. Ciofalo, Multi-physical modelling of reverse electrodialysis, Desalination. 423 (2017) 52–64. doi:10.1016/j.desal.2017.09.006.
- [60] S. Mikhaylin, L. Bazinet, Fouling on ion-exchange membranes: Classification, characterization and strategies of prevention and control, Adv. Colloid Interface Sci. 229 (2016) 34–56. doi:10.1016/j.cis.2015.12.006.
- [61] L. Bazinet, T.R. Geoffroy, Electrodialytic Processes: Market Overview, Membrane Phenomena, Recent Developments and Sustainable Strategies, Membranes (Basel). 10 (2020) 221. doi:10.3390/membranes10090221.
- [62] M.A.C.K. Hansima, M. Makehelwala, K.B.S.N. Jinadasa, Y. Wei, K.G.N. Nanayakkara, A.C. Herath, R. Weerasooriya, Fouling of ion exchange membranes used in the electrodialysis

- 772 reversal advanced water treatment: A review, *Chemosphere*. 263 (2021) 127951.
 773 doi:10.1016/j.chemosphere.2020.127951.
- 774 [63] D.A. Vermaas, D. Kunteng, M. Saakes, K. Nijmeijer, Fouling in reverse electrodialysis under
 775 natural conditions, *Water Res.* 47 (2013) 1289–1298. doi:10.1016/j.watres.2012.11.053.
- 776 [64] D.A. Vermaas, D. Kunteng, J. Veerman, M. Saakes, K. Nijmeijer, Periodic feedwater reversal
 777 and air sparging as antifouling strategies in reverse electrodialysis, *Environ. Sci. Technol.* 48
 778 (2014) 3065–3073. doi:10.1021/es4045456.
- 779 [65] M. La Cerva, M. Di Liberto, L. Gurreri, A. Tamburini, A. Cipollina, G. Micale, M. Ciofalo,
 780 Coupling CFD with a one-dimensional model to predict the performance of reverse
 781 electrodialysis stacks, *J. Memb. Sci.* 541 (2017) 595–610. doi:10.1016/j.memsci.2017.07.030.
- 782 [66] G. Battaglia, L. Gurreri, G. Airò Farulla, A. Cipollina, A. Pirrotta, G. Micale, M. Ciofalo,
 783 Membrane Deformation and Its Effects on Flow and Mass Transfer in the Electromembrane
 784 Processes, *Int. J. Mol. Sci.* 20 (2019) 1840. doi:10.3390/IJMS20081840.
- 785 [67] G. Battaglia, L. Gurreri, A. Cipollina, A. Pirrotta, S. Velizarov, M. Ciofalo, G. Micale, Fluid–
 786 Structure Interaction and Flow Redistribution in Membrane-Bounded Channels, *Energies*. 12
 787 (2019) 4259. doi:10.3390/EN12224259.
- 788 [68] G. Battaglia, L. Gurreri, M. Ciofalo, A. Cipollina, I.D.L. Bogle, A. Pirrotta, G. Micale, A 2-D
 789 model of electrodialysis stacks including the effects of membrane deformation, *Desalination*.
 790 500 (2021) 114835. doi:10.1016/j.desal.2020.114835.
- 791 [69] G. Battaglia, L. Gurreri, G.A. Farulla, A. Cipollina, A. Pirrotta, G. Micale, M. Ciofalo,
 792 Pressure-induced deformation of pillar-type profiled membranes and its effects on flow and
 793 mass transfer, *Computation*. 7 (2019) 1–14. doi:10.3390/computation7020032.
- 794 [70] E. V. Laktionov, N.D. Pismenskaya, V. V. Nikonenko, V.I. Zabolotsky, Method of
 795 electrodialysis stack testing with the feed solution concentration regulation, *Desalination*. 151

- 796 (2003) 101–116. doi:10.1016/S0011-9164(02)00988-8.
- 797 [71] M.S. Isaacson, A.A. Sonin, Sherwood Number and Friction Factor Correlations for
 798 Electrodialysis Systems, with Application to Process Optimization, 1976.
 799 doi:10.1021/i260058a017.
- 800 [72] S.S. Islam, R.L. Gupta, K. Ismail, Extension of the Falkenhagen-Leist–Kelbg Equation to the
 801 Electrical Conductance of Concentrated Aqueous Electrolytes, *J. Chem. Eng. Data.* 36 (1991)
 802 102–104. doi:10.1021/je00001a031.
- 803 [73] E. Volodina, N. Pismenskaya, V. Nikonenko, C. Larchet, G. Pourcelly, Ion transfer across ion-
 804 exchange membranes with homogeneous and heterogeneous surfaces, *J. Colloid Interface Sci.*
 805 285 (2005) 247–258. doi:10.1016/j.jcis.2004.11.017.
- 806 [74] M.B. Kristensen, A. Bentien, M. Tedesco, J. Catalano, Counter-ion transport number and
 807 membrane potential in working membrane systems, *J. Colloid Interface Sci.* 504 (2017) 800–
 808 813. doi:10.1016/j.jcis.2017.06.010.
- 809 [75] N.D. Pismenskaya, E.D. Melnikova, O.A. Rybalkina, V. V. Nikonenko, The Impact of Long-
 810 Time Operation of an Anion-Exchange Membrane AMX-Sb in the Electrodialysis
 811 Desalination of Sodium Chloride Solution on the Membrane Current–Voltage Characteristic
 812 and the Water Splitting Rate, *Membr. Membr. Technol.* 1 (2019) 88–98.
 813 doi:10.1134/s2517751619020070.
- 814 [76] V. Sarapulova, I. Shkorkina, S. Mareev, N. Pismenskaya, N. Kononenko, C. Larchet, L.
 815 Dammak, V. Nikonenko, Transport characteristics of fujifilm ion-exchange membranes as
 816 compared to homogeneous membranes AMX and CMX and to heterogeneous membranes
 817 MK-40 and MA-41, *Membranes (Basel)*. 9 (2019) 84. doi:10.3390/membranes9070084.
- 818 [77] A. Culcasi, L. Gurreri, A. Zaffora, A. Cosenza, A. Tamburini, A. Cipollina, G. Micale, Ionic
 819 shortcut currents via manifolds in reverse electrodialysis stacks, *Desalination*. 485 (2020)

- 820 114450. doi:10.1016/j.desal.2020.114450.
- 821 [78] M. La Cerva, L. Gurreri, M. Tedesco, A. Cipollina, M. Ciofalo, A. Tamburini, G. Micale,
822 Determination of limiting current density and current efficiency in electrodialysis units,
823 Desalination. 445 (2018) 138–148. doi:10.1016/j.desal.2018.07.028.
- 824 [79] O.A. Kozaderova, K.B. Kim, C.S. Gadzhiyeva, S.I. Niftaliev, Electrochemical characteristics
825 of thin heterogeneous ion exchange membranes, J. Memb. Sci. 604 (2020) 118081.
826 doi:10.1016/j.memsci.2020.118081.
- 827 [80] F. Dong, D. Jin, S. Xu, L. Xu, X. Wu, P. Wang, Q. Leng, R. Xi, Numerical simulation of flow
828 and mass transfer in profiled membrane channels for reverse electrodialysis, Chem. Eng. Res.
829 Des. 157 (2020) 77–91. doi:10.1016/j.cherd.2020.02.025.

830