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Ion-exchange membrane reinforcing

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ABSTRACT

Sufficient mechanical property of ion-exchange membrane is a key factor for its successful implementation to electrodialysis (ED) stack. Although the ED is not a pressure driven process, the membrane need to withstand some small overpressure and also manipulation during stack assembling. In this work, the use of short polypropylene and glass fibers as low cost alternative to common woven or nonwoven fabric was studied. We confirmed that short polypropylene fibers rapidly increase the mechanical strength in machine direction (MD) even at very low concentration.

Keywords: Ion-exchange membrane reinforcing; Fabric; Short fiber

1. Introduction

Although electrodialysis (ED) or electrodeionization (EDI) are not a pressure driven process, the ion-exchange membranes need sufficient mechanical properties not only during stack building but also during process. The reason is possibly small (for ED) or higher (for EDI) overpressure between dilute and concentrates, stack pressure and pressure drop over the stack. In case of insufficient mechanical properties, the membrane can deform and some cracks may occur.

Mechanical properties of both homogeneous and heterogeneous ion-exchange membrane are rather poor. The reason is small thickness or very brittle homogeneous material or high resin content and poor interaction between the components for heterogeneous membranes. Therefore, these membranes need to be reinforced for the improvement of their mechanical properties, in particular of their tensile strength. The several fabric types can be used for reinforcing according to the application: polyester, polypropylene, and acrylic fabric. For special applications, some other polymers may be used, such as a chemically stable and temperature-stable polyether ether ketone.

Also presence of fabric rapidly decrease areal dimension changes during swelling and during ionic form changes. Further, reduced water content, which causes additional porosity, slightly decreases permselectivity [1]. In Table 1, there is comparison of heterogeneous membrane's mechanical properties and their swelling and electrochemical properties.

An incorporation of chopped fibers instead of a common woven or nonwoven fabric appears to be one of the good solutions for increasing the membrane mechanical properties [2]. The aim of this work was to

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Table 1
Mechanical and electrochemical properties of swelled membrane and membrane foil

Membrane type	Young's modulus E (MPa)	Tensile strength σM (MPa)	Elongation εM (%)	Swelling (%)		Water content (wt %)	Specific resistance R_S (Ω cm)	Permselectivity P (%)
				Thickness	Areal			
Ralex PES	150	12	25	50–60	2–3	33–37	100–120	91–93
Membrane foil	20	3	150	25–30	15–20	39–43	100–120	88–90

Note: These are typical property values and no warranties of such value are given.

prepare cation exchange membranes with incorporated glass or polypropylene chopped fibers.

2. Theoretical background

Behavior of fiber reinforced polymer composites is very important for modeling and composite optimization. The interaction between fibers and matrix are extremely complex especially when other particles are present. The first attempt to explain the reinforcing effect was entirely based on elastic interaction. Now, this theory is referred as the shear lag theory which is continuously refined [3]. On the basis of this theory, we are able to calculate average fiber stress by following Eq. (1), where E is Young's modulus, ε is the deformation, $s = l/d$ represents fiber aspect ratio, n is a dimensionless parameter which include mechanical properties of matrix and fibers and also fiber concentration. The function in the brackets show how much stress could be transferred between matrix and fibers.

$$\bar{\sigma} = E_f \cdot \varepsilon_f \cdot [1 - \tanh(ns)/ns] \tag{1}$$

From the following Fig. 1, there is an example of HPDE composite with only 3 vol% of glass fiber with 12 μm diameter. In case of fiber aspect ratio at 100 (fiber length 1.2 mm), the 65% of fiber stress could be transferred to matrix. The more the fiber concentration, the more stress is transferred to matrix. This shows that even short fiber is sufficient and long fibers are not needed. The short fibers are mostly promised in case of their low concentration in composite due to better distribution.

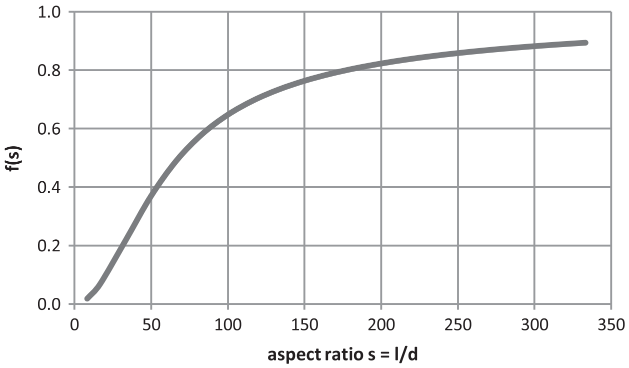

Fig. 1. Dependence of stress transfer index f(s) on fiber aspect ratio.

3. Experimental

3.1. Membrane sample preparation

For our experiment, we used glass fiber (14 μm in diameter and 12 mm in length) and polypropylene fibers (18 μm in diameter and 12 mm in length). In the laboratory, two roll calendar, the basic mixture with 60 wt% of cation resin, and 40 wt% of LLDPE was prepared. To this mixture 5–25 rel wt% of polypropylene or 10–50 rel. wt% of glass fibers was added. Then, the thin membrane foil was pulled off. Due to high density of glass, the higher relative wt% of fibers need to be used to reach similar volume concentration.

3.2. Fiber distribution determination

For optical analysis of fiber distribution, orientation, and length, we used electron microscope VEGA Tescan in SEM mode. For this analysis, the dry sample was used. For analysis of swelled membrane, the ESEM mode need to be used. In this mode, the picture, obviously, is not so sharp and therefore the optical analysis is not so precise.

3.3. Mechanical properties

Due to primary orientation of fibers in machine direction (MD), we measured the basic mechanical properties (Young's modulus, tensile strength, and elongation) in transverse direction (TD). For this measurement, the Instron 5800 was used according to method ČSN EN ISO 527 type specimen 5. The speed of deformation was set up on 10 mm/min. The mechanical properties was measured on totally swelled samples, e.g. in their working condition. This is more important than measurement in dry form. The swelling obviously decreases Young's modulus and tensile strength, while elongation increases due to increasing of composite elasticity. In Fig. 2, there is typical stress–strain curve. In most cases, the elastic deformation is nearly linear. After the yield point, the stress can increase or decrease, so the different behavior can occur depending on polymer and filler type including particle size distribution and concentration. For our mechanical properties, determination of the tensile strength and the elongation at break point were used.

3.4. Electrochemical properties

Both electrochemical resistances (areal R_A and specific R_S) of investigated membranes were determined by a standard potentiometric compensation method [4]. The electrochemical resistance for compensation method is calculated by the following Eqs. (2) and (5), where R_j^s is the resistance without membrane, R_j^s is the resistance with membrane, and R_{Aj} is the areal resistance of membrane, U_{meas} is the measured potential under the current, U_{as} is the asymmetric potential measured without applied current, A_m is the active sample area, Th_j is the sample thickness, index s is the solution, m is the membrane, and j is the solution type. The (1, 2) and (2, 1) means sequence of saturated calomel electrode (SCE). For our measurement, the 0.5 M NaCl was used.

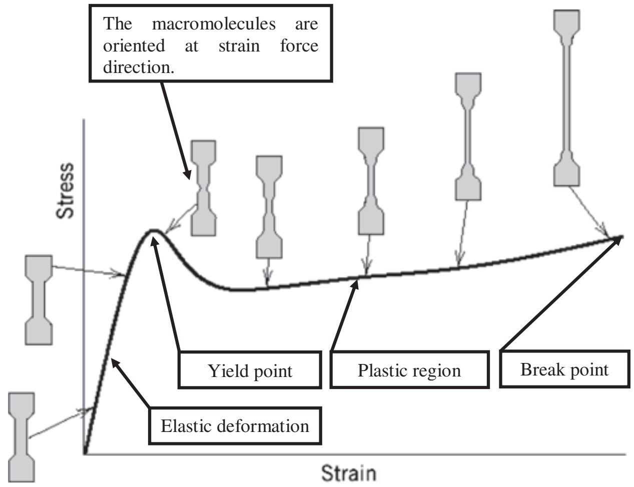

Fig. 2. Typical stress–strain curve.

$$R_j^s = \frac{\left|U^s_{meas.}(1,2) - U^s_{as}(1,2)\right|_j + \left|U^s_{meas.}(2,1) - U^s_{as}(2,1)\right|_j}{2I} \tag{2}$$

$$R_j^{s+m} = \frac{\left|U^{s+m}_{meas.}(1,2) - U^{s+m}_{as}(1,2)\right|_j + \left|U^{s+m}_{meas.}(2,1) - U^{s+m}_{as}(2,1)\right|_j}{2I} \tag{3}$$

$$R_{A,j} = \left(R_j^{s+m}(1) - \bar{R}^s\right)A_m \tag{4}$$

$$R_{S,j} = \frac{R_{Aj}}{Th_j} \tag{5}$$

Permselectivity (or transport number) is determined by using the same cell as for electrochemical resistance but without applied electric current. The principle of this static method is based on Henderson's equation which determines the transport number under diffusion [5]. The experimental cell is separated into two parts by IEM. Every part contains a solution with different concentration. For our measurement, the 0.1/0.5 M KCl and Ag/AgCl reference electrode were used at 25°C. The following Eqs. (6) and (7) were used for permselectivity calculation, where $\gamma_\pm$ is the activity coefficient and m_s is the molality of solution 1 (0.1 M KCl) and solution 2 (0.5 M KCl).

$$E_{M\,theor}(V) = -\frac{RT}{zF}\cdot\ln\left(\frac{\gamma^2_{\pm,1}\cdot m^2_{S,1}}{\gamma^2_{\pm,2}\cdot m^2_{S,2}}\right) \tag{6}$$

$$P_K^M(\%) = \frac{E_{M\,meas}}{E_{M\,theor}}\times 100\% \tag{7}$$

4. Results and discussion

4.1. Fiber distribution

On the basis of the optical analysis, we found that brittle glass fibers were broken from 12 mm to approx. 20–700 microns (aspect ratio 1.4–50), while more flexible PP fibers were broken to approx. 200–1,000 microns (aspect ratio 11–55). The fibers longer more than 150–200 microns are oriented by MD while short fibers are oriented in all directions (see Fig. 3). Due to high melt temperature and high mechanical strength, the glass fibers keep the circular shape while PP fibers are little bit deformed.

In both cases, the fibers length in composite is more than 10 times shorter than its original length. The reason is high shear, low temperature, and kneading mechanism of calendaring. We suppose the usage of more gentle mixing technique (two or single

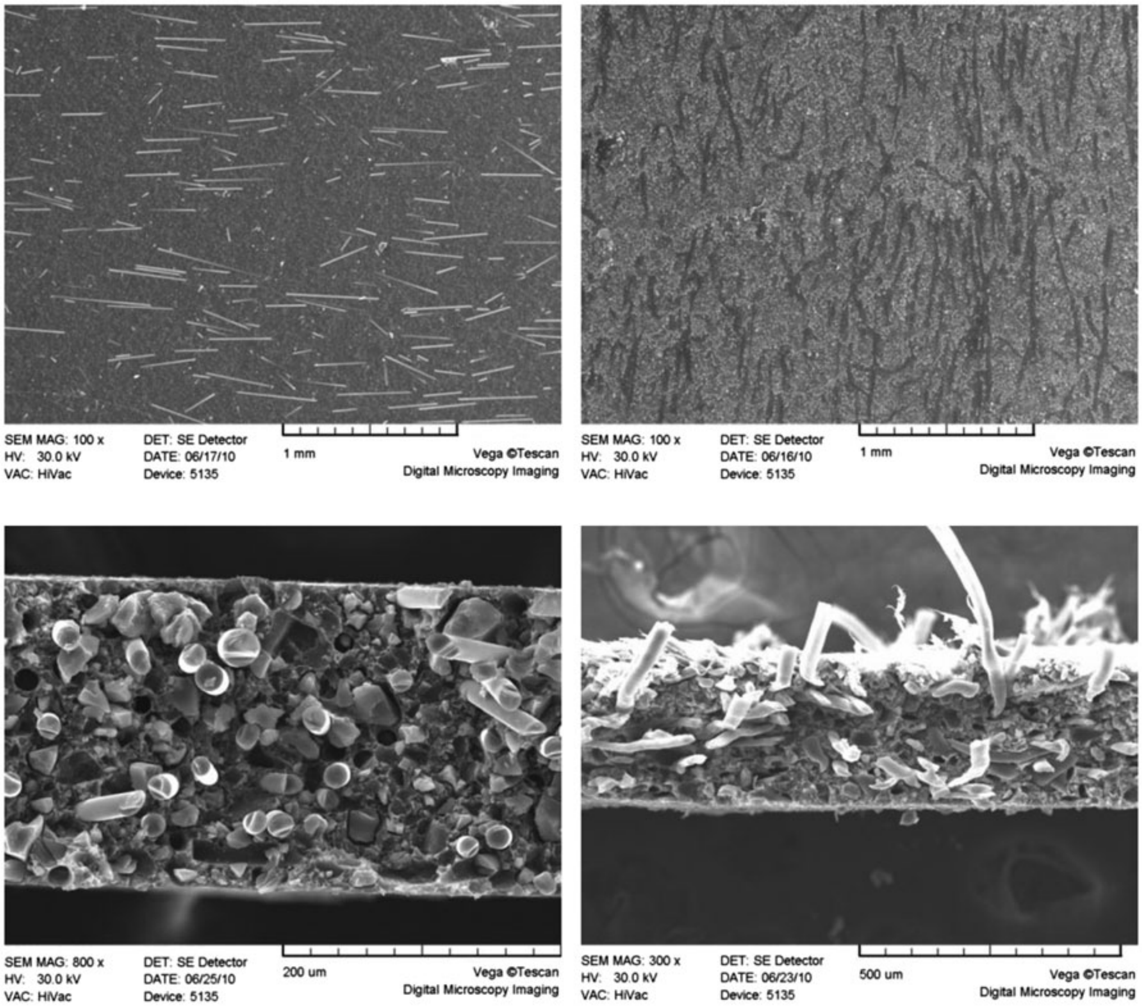

Fig. 3. Microphotograph of glass (left) and PP filled (right) membrane composite, 25 rel wt% of fibers, surface (top), break (bottom).

screw kneaders) could keep the maximum fibers length (maximum aspect ratio) and could improve mechanical properties.

4.2. Mechanical properties

If we compare mechanical properties of membranes with glass or PP fibers on Fig. 4 we need to say that the PP fibers are much effective. We suppose the reason of weak mechanical properties of membrane with glass fibers is loss of adhesion due to fiber surface hydrolysis. The other reason could be too low fiber length. According to Fig. 1, very short fibers cannot transfer so much stress as long fibers. These short fibers act like inert filler which decreases mechanical properties.

Except the direct measurement of mechanical properties, we also measure dimension stability during swelling. These measurements also reflect the mechanical properties. The lesser the dimension changes during swelling, the higher the tensile strength will be. In Table 2, there is a comparison of standard laminated membrane CM-PES, membrane foil CF and membrane foil with PP (CF-PP) or glass fibers (CF-GF). The results confirmed very good PP fiber reinforcing effect, especially in MD (length). High impact of fiber content on swelled difference in thickness or width was not observed.

4.3. Electrochemical properties

Finally, we compare the electrochemical properties like specific resistance and permselectivity. Also, these measurements confirmed very good results of PP fiber modified membrane foil. As we expect with increasing fiber content the specific resistance also increase. The

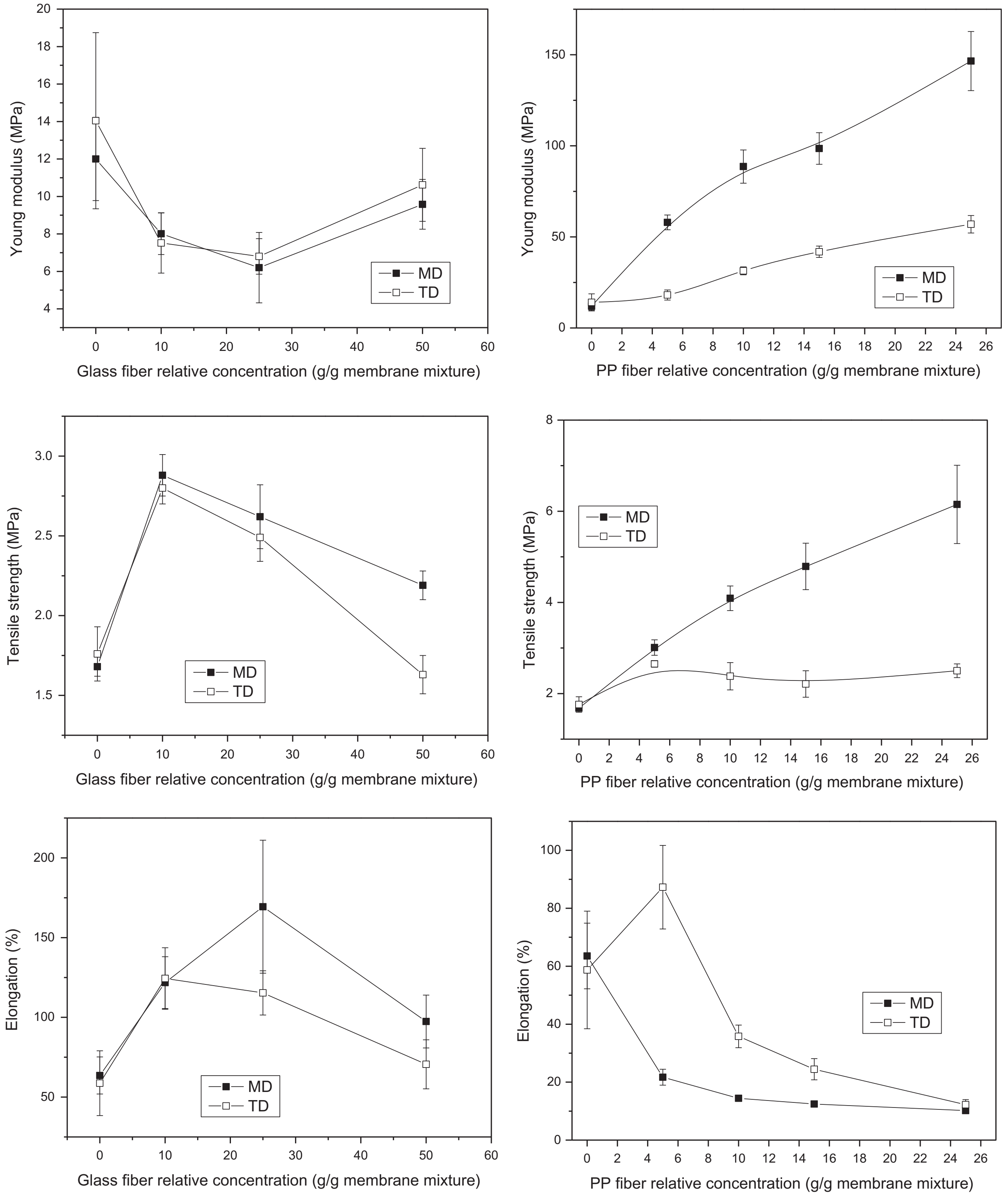

Fig. 4. Mechanical properties of swelled membrane. Dependence of Young modulus, tensile strength and elongation on glass fiber (left) and polyproplyne fiber (right) relative concentration.

Table 2
Electrochemical properties of laboratory samples

	Fiber concentration		Swelled differences Δ (in demi-water)[a]				Specific resistance R_S (Ω cm)	Permselectivity P (%)
Membrane type	(rel. wt%)	(total vol%)	Δt (%)	Δl (%)	Δw (%)	Δwt (%)		
CM-PES	10.2[b]	8.9[b]	58.7	2.2	3.0	58.6	105.3	95.1
CF	–	–	30.5	19.9	21.6	80.2	50.5	91.3
CF-PP	5	6.8	37.5	6.0	18.8	64.8	68.5	92.2
	10	12.8	41.8	3.0	18.8	62.2	84.9	92.6
	15	18.0	42.8	2.0	17.3	56.7	90.3	92.7
	25	26.8	41.7	1.5	12.7	51.6	106.2	92.6
CF-GF	10	4.7	25.7	16.6	18.9	64.6	67.0	91.6
	15	6.9	24.8	16.6	18.4	59.1	71.9	92.1
	25	11.0	23.5	15.0	18.4	54.7	75.5	90.5
	50	19.7	29.0	13.6	19.8	52.3	76.3	90.7

[a] Relative changes between swell and dry membrane in thickness (t), length (l), width (w), and weight (wt).

[b] Fabric concentration equivalent.

permselectivity of CF-PP is also slightly better than pure membrane foil but still low in comparison to laminated membrane.

Results of glass filled membrane foil are worse than pure membrane foil. There are some slight benefits of better dimension stability, but at the expenses of higher specific resistance and lower permselectivity.

5. Conclusions

In this work, alternative reinforcing technique for heterogeneous ion-exchange membranes by using short fibers was investigated. For our experiment, the glass and polypropylene fibers were used. We confirmed that using of PP short fibers improve tensile strength, especially in MD. Even very short amount of PP fibers can rapidly increase mechanical strength in MD. We also confirmed that using woven fabric laminated on both membrane side provide ultimate reinforcing characteristics but at the expense of increasing the price. Because electro dialysis process does not need such high mechanical stability, using short fibers could be very promising and cheap alternative. Membrane foil with short fibers could be very useful for membranes where using fabric is impossible or is limited, for example hollow fiber ion-exchange membrane for diffusion dialysis. Profiled membrane is other application due to limited thermoforming abilities of laminated membrane.

Acknowledgments

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References

[1] P.V. Vyas, S.K. Adhikary, Studies on heterogeneous cation-exchange membranes, React. Funct. Polym. 44 (2000) 101–110.

[2] T. Bárány, J. Karger-Kocsis, Development and characterization of self-reinforced poly(propylene) composites: Carded mat reinforcement, Polym. Adv. Technol. 17 (2006) 818–824.

[3] M.R. Piggott, Load-Bearing Fibre Composites, International Series on the Strength and Fracture of Materials and Structures, Pergamon, Oxford, 1980, ISBN: 0-08-024230-8.

[4] G. Lencová, V. Kysela, J. Vladařová, Laboratory Control of Ion Exchange Membrane Production Process, Permea 2009, Prague, June 7–11, 2009.

[5] J. Koryta, J. Dvorak, L. Kavan, Principles of Electrochemistry, second ed., John Wiley & Sons, Chichester, 1993.