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Optimizing porous material in shock electrodialysis unit

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ABSTRACT

Shock electrodialysis (SED) is a new electromembrane process for water desalination. The principle is similar to electrodeionization – the product should be ultrapure water, but the inlet water can be the same quality as the inlet to electrodialysis. The ion exchange resin is substituted by porous media and used ion exchange membranes are just of one type (i.e., two cation exchange membranes or two anion exchange membranes). The use of porous media is essential. Many physical and chemical phenomena including electroosmotic flow, electroconvection, surface conduction combined in the moment lead to the phenomena of a "–shock wave" and SED, respectively. The mechanism of the wave is represented by the formation of a sharp border in the water stream between the highly concentrated and ion-free zone. The whole process was studied by Prof. Martin Bazant's group at MIT, Department of Chemical Engineering. The aim of this particular study is characterization and experimental testing of porous material as an essential component of SED. A variety of organic and synthetic porous materials were tested by various analytical methods and in the SED laboratory unit itself. The work reports an overview of commonly available and appropriate materials analogous to the glass frit used in the first prototypes developed by Bazant's group. Considering the physical properties and behavior in experimental conditions and based on the results exhibiting stable desalination, we suggest the optimal porous material as well as the housing for this media. Finally, it is represented by quality of products, hydrodynamic resistance, prize of the porous material, availability and also by workability (machinability) for appropriate shape and also construction stability.

Keywords: Water treatment; Shock electrodialysis; Porous media; Desalination

1. Introduction

Water resources are essential not only for the life but also for the energy mass production as well. The biggest concern may not come from the overall amount of water on earth but from clarity and availability of the water resources as well.

Current state-of-the-art water treatment is determined by membrane processes. There is probably no whole new, competitive process for the near future, but there is still room for optimization and development of nowadays well-known membrane processes. Close to the physical and thermo dynamical limits of the membrane processes we can revise the whole design and principles based on the current knowledge and use of nanotechnologies and use it with an advantage. While the majority of the water resources on the Earth naturally occurs in the form of sea and brackish waters and while the mass energy and industrial production requires huge volumes of ultrapure water (as close to theoretical water as possible), very important and effective

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methods for water treatments are nowadays desalination processes, including electrodialysis and electrodeionization. However the operational costs play important role in the industrial utilization. Electrodialysis, which uses pairs of alternating cation and anion exchange membranes ordered in a stack between two electrodes for effective separation of ions from the inlet, finds its limits in poorly desalinated outlet, reaching at best values in the order of hundreds of milligrams per liter. This limitation comes from conductivity of the diluate getting too low (under 0.1 mS cm^{-1}) and resistance high enough for the process to become ineffective for the ion separation. Electrodeionization solves this problem by filling the diluate and in special circumstances even concentrate chambers with granular ion exchanger, which rises effectively the conductivity of the inner environment of the stack, allowing for desalination of water of even lower salinity than in the case of electrodialysis. Nevertheless, both of these processes require pre-treated water and the desalination is limited by diffusion, where the limiting current arises from concentration polarization at the membrane.

This paper focuses on the electromembrane method called shock electrodialysis (SED) which moves the electrodialysis process far forward by theoretically exceeding the limiting current and reaching over-limiting conductance. Its theoretical potential is represented by effective one-step desalination ("shock desalination") with an electrodialysis stack assembled from just one type of membrane (e.g., cation or anion exchange membrane) and the space between them filled with porous material. The method theoretically allows for very complex water treatment including filtration and disinfection, as described in the study by Bazant et al. [1]. The theoretical principles are already studied, mathematically modelized and experimentally confirmed by the Bazant's group at MIT, but for the future industrial scale-up a lot of work needs to be done. In this paper we take a closer look at the major component of the SED unit – porous media.

2. Theory

Ion concentration polarization is a gradient of the ion concentration near perm-selective membrane [2]. The presence of the following phenomena is now believed to be the mechanism for the over-limiting current: water-splitting (chemical process producing additional ions), electroosmotic instability (physical process resulting in enhanced ion transport by current induction) and surface conduction [3–7]. Frilette [8] proved, that water-splitting plays a minor role. Much more important charge carriers are counterions thanks to the current-induced convection.

In SED unit, the porous media adheres to a pair of ion-exchange membranes and fills the whole volume between the membranes in 1-chamber electrodialysis unit. When we look at the whole process of shock desalination chronologically, the desalination is initiated by the perm-selective membrane and the depleted region ("diluate") adjacent to the membrane is spread in the micro-nanostructured porous media. This is possible because of the presence of inhomogeneous space charge region in the channels inside the media created by normal component of the applied electrical field. The current is conducted by the ions cumulated along the curved channels with the electrical double layers formed at the walls [3,4,6,7,9,10]. By this mechanism, we obtain a sharp concentration gradient propagating through the channels of the medium (Fig. 1). Extension of one-dimensional equation for thin electrical double layer and shock propagation [11,12] describes mathematically a shock distribution in the concentration profile.

According to mathematical computation by Dydek et al. [4], the charge density of the porous media should range from 1% to 10%. The II generation SED unit operated by Schlumpberger [10] used the glass frit with the charge density ranging from 2.3% to 62% (5.99×10^4 C m^{-3} and 2.21×10^5 C m^{-3}). Regarding the used membranes (or membrane-less process), nano-micro channels in diameter, magnitude of applied current, axial diffusion, etc., there are no limits [11] – the pores should only be significantly smaller than the flow-through of the porous medium [10].

3. Experimental settings

3.1. II and III generation of SED unit design and apparatus

The starting point for the SED unit design was a prototype constructed at MIT by Martin Bazant's group [1,10] – let's call it II generation unit (I. generation unit was "the button unit" [10]). This unit was reconstructed and after initial proving experiments scaled-up to III generation unit. Recently, the IV generation unit was tested and will be briefly described separately in discussion, chapter 4.4.

Casing was composed of four parts made up of transparent material – polycarbonate (PC) and later of polyvinylchloride (PVC) (III generation unit). The internal frame is a U-shape housing for the porous medium and reservoir

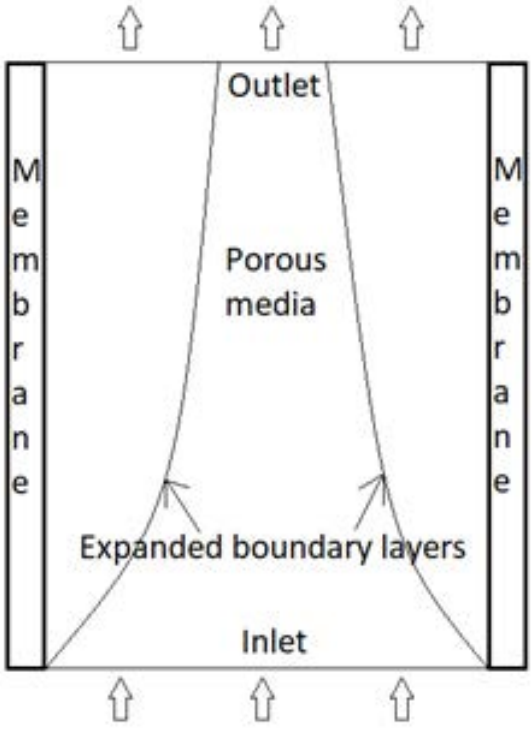

Fig. 1. Boundary layer expansion in porous media.

where two identical cation-exchange membranes (Nafion 117/115 or Ralex CF-R-14) are adjacent from each side to the negatively charged porous medium. Porous medium in sandwich with ion exchange membranes was inserted between two side plates with housing for electrodes (Fig. 2). Electrodes were made of titanium mesh (60 mesh woven from 0.2 mm dia wire, Alfa Aesar, Kandel, Germany) connected to titanium wires (0.25 mm dia wire 99.99% Alfa Aesar, Kandel, Germany). The fourth part is a head plate with an implemented separator for diluate and concentrate. The whole unit was sealed using soft GORE GR Sheet Gasketing. The III generation was sealed also using standard rubber.

Porous media shaping: Selected porous media were shaped to fit into its frames precisely and inserted into the internal frame using two-component epoxy resin (BISON Epoxy glue). The porous media dimensions were 20 mm × 10 mm × 3 mm (II generation) and 40 mm × 40 mm × 10 mm (III generation).

Pumps and solution: stable inlet of 0.01 M Na_2SO_4 was pumped with three 60 mL syringes using SyringePump NE-1000. During longer experiments, syringe pumps were replaced by peristaltic pumps (Czech Company Kouřil, Ltd., Kyjov) PCD 61.4 (two channel) for catholyte and anolyte and PCD 82S for pumping inlet solution from a large reservoir (starting at 50 L).

3.2. Voltage source, measuring equipment and software

The experiments were carried out in a chronoamperometry mode using potentiostat Bio-Logic SP-300 (for II generation units) and Biologic SP-150 (III generation unit). Software used by Bio-Logic devices is EC-LAB, version V10.44 (SP-300) and V11.18 (SP-150). The product was monitored online by WTW Cond 3310 with WTW TetraCon 25 measuring cell. Applied voltages were 5–15 V for II generation unit, 5–8 V for III generation unit.

3.3. Porous media selection

The first material selection for the II generation unit included originally used fine structured glass frit (Adam & Chittenden Scientific Glass, Brekeley, CA 94710) and after approval of the function of the unit a high-quality Porotherm brick was used as a random, available and extremely cheap porous material. Other materials used in II generation modules were ceramics Pormulit C530 from CeramTec Ltd., Šumperk Composed of 70% Al_2SO_3 and SiO_2. In III generation unit first selected material was silica ceramics C510. Very promising material was extremely porous material, mechanically similar to chalk, composed of xonolite $C_6Si_6O_{17}(OH)_2$ and tobermorite $C_5Si_6O_{16}(OH)_2$ with glass fiber as admixture. The last tested material was again a high quality, very dense hollow brick used as a roof fitting (Hurdis, Wienerberger Ltd., České Budějovice) with pore distribution very similar to glass frit (Graph 1, Graph 2).

Pore size distributions and porosity of the selected materials were determined using an AutoPore IV 9500 intrusion porosimeter (Micromeritics, Norcross, GA 30093-2901, U.S.A.) at The University of Chemistry and Technology in Prague and an AutoPore IV 9510 mercury intrusion porosimeter (Micromeritics, Norcross, GA 30093-2901, U.S.A.), which operates with pressures from 0.01 to 414 MPa. A region was evaluated, quantitatively corresponding to the pore size 3.2 – 810,000 nm for all samples (full measurement range). Other characteristics including hydrodynamic resistance, liquid erosion resistance and

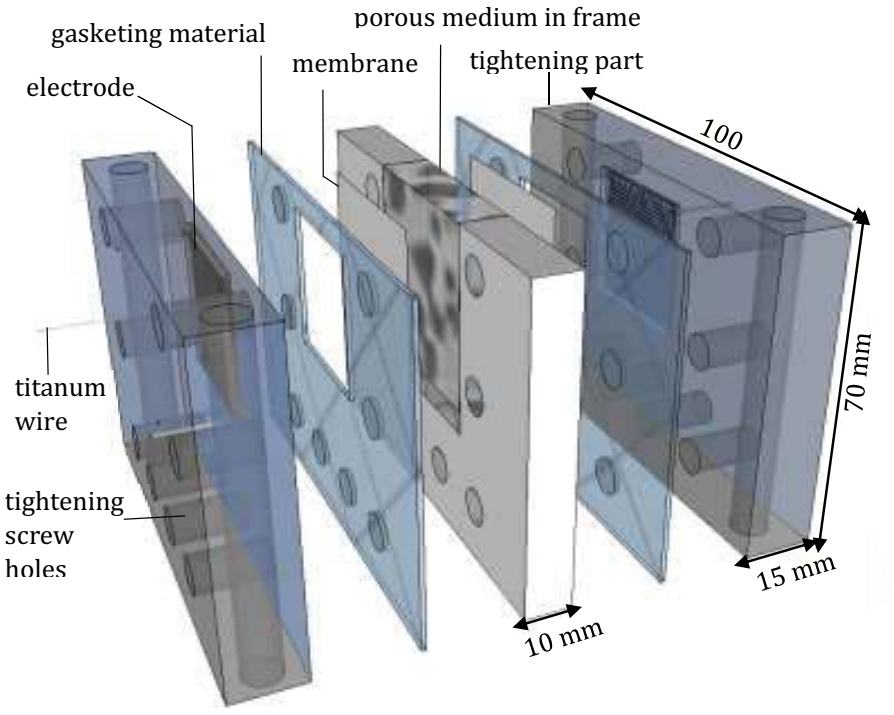

Fig. 2. III generation unit prototype of shock electrodialysis.

chronoamperometry characterization during operation are discussed in 4th chapter.

4. Results and discussion

4.1. Flow rate

Pore distribution, porosity and pore diameters influence directly maximum flow rates through the medium. The glass frit of 30% porosity and the other similar materials (Table 1) report high hydrodynamic resistivity of top flow rates up to 0.3 mL min^{-1} (maximum pressure given by peristaltic pump was 50 kPa, i.e., 7.25 psi). Significantly higher flow rates of approximately 1.3 mL min^{-1} were reached with tobermorite and xonolite mixture material which porosity was 90%.

4.2. Mechanical stability

Experiments revealed the importance of the mechanical stability of the porous material. The porous component must be precisely processed to its required shape and precisely embedded in the internal frame. The porous media also needs to be stable from a long-term usage perspective where higher pressures may be applied. Ceramics is very stable and inert, but on the other hand it is very hard and fragile, which brings problems with shaping. The appropriate or inappropriate properties of the material are revealed after several hours of operation in SED unit. These experiments showed that xonolite/tobermorite mixture was destroyed by erosion (Fig. 6) after several hours of operation.

Table 1
Characterization of porous materials

Supplier	Material type	Product name	Typical pore diameter (nm)	Porosity (%)
VUSTAH	Xonolite & tobermorite mixture		313	90
Wienerberger (České Budějovice)	Fired brick	Porotherm	17,891 and 418	33
	Silica ceramics	Pormulit® C530	?	?
CeramTec (Šumperk)	Silica ceramics	C510	843	33
	Fired brick Hurdis		844	35
Adam & Chittenden Scientific Glass (Brekeley, CA 94710)	Glass frit	Ultra Fine	843	31

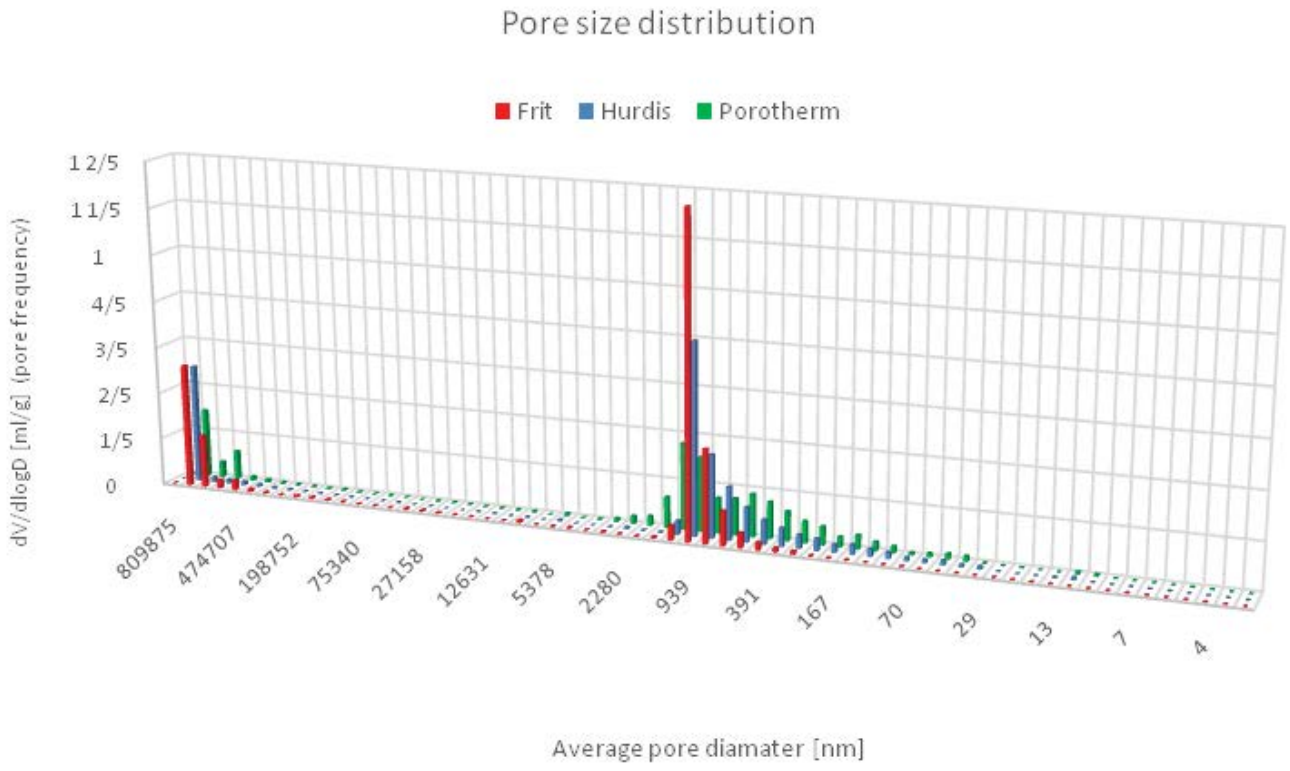

Fig. 3. Histogram of porous samples – Frit, Hurdis, Porotherm. Mercury porosimetry measured at The Unipetrol Centre for Research and Education (AutoPore IV 9510).

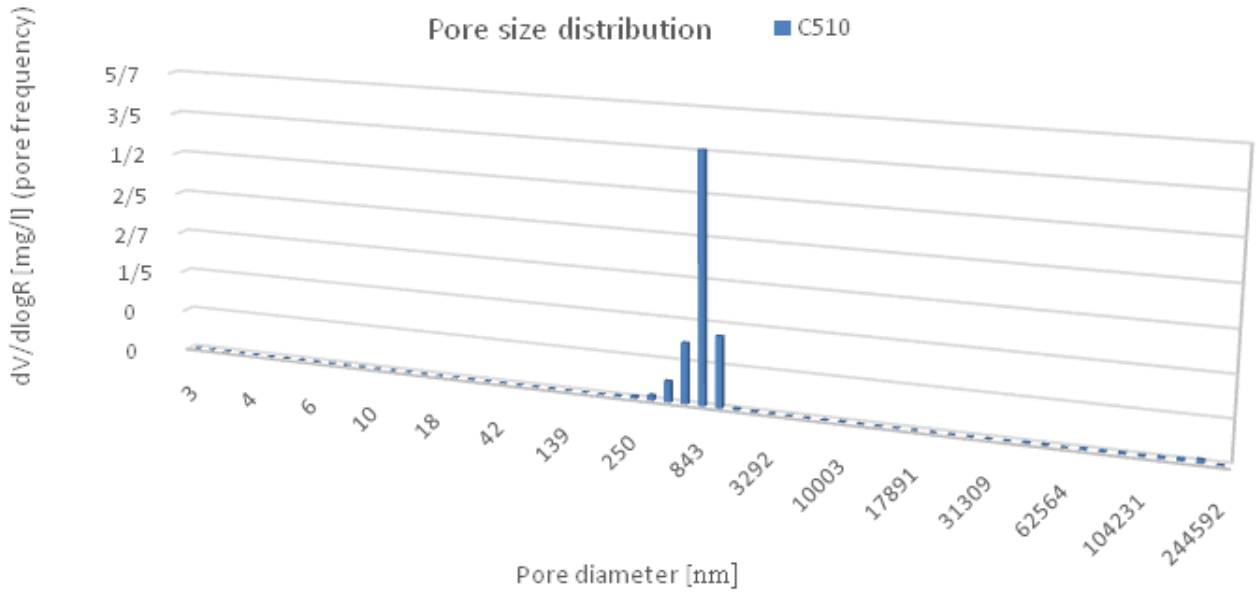

Fig. 4. Histogram of sample – Ceramtec Pormulit C510. Mercury porosimetry measured at University of Chemical Technology, Prague (Micromeritics Autopore IV 9500, Norcross, GA 30093-2901, U.S.A.).

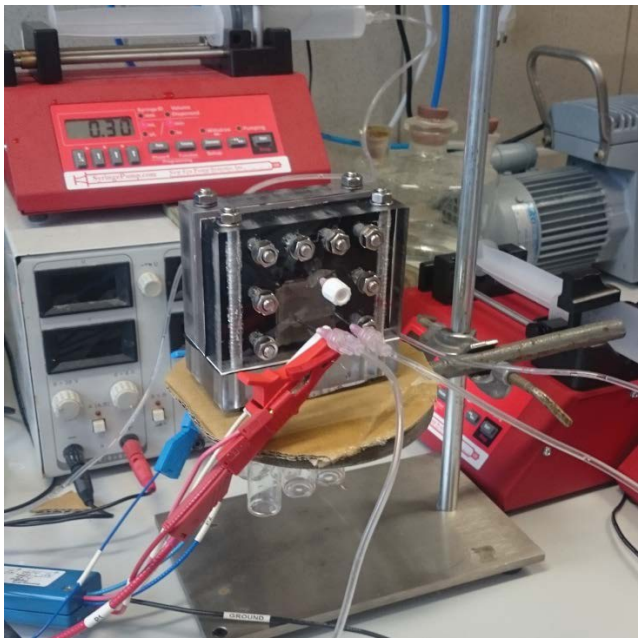

Fig. 5. Experimental settings and the whole apparatus – III generation unit of shock electrodialysis.

4.3. Chronoamperometry and desalination results

According to the theory, a stable desalination hand in hand with a stable electrical current was expected. In the beginning of the experiments (a few minutes) the current stabilization differs for various porous media. A unit with glass frit, Nafion membranes shows stable 30%–40% desalination at the outlet with different current curves through various experiments while maintaining the same conditions. Fig. 7a shows an example of this situation with applied voltage 13.5 V. With III generation unit, very similar effects were present. Fig. 7b shows III generation unit with C510 material, 7 V applied and Nafion 115/117 membranes. The conductivity of inlet solution dropped by 40% with both red and blue experiments. At this outlet, the pH of the solution for C510 material dropped from 7 (at the inlet) to approximately 6, which correlates with expectation.

Stable current was achieved over time by testing tobermorite and xonolite mixture in III generation unit. Applying different voltages ranging from 5 to 9 V every time led to a stable current over several hours of experiments with little different stabilization times responding to current condition of unit (Graph 3b). However, there was neither stable desalination measured with this material (Table 3) nor pH differences at inlet and outlet.

With Hurdis material applied in III generation unit, the desalination was not obtained nor any changes in pH in the outlet vs. inlet. However, separation proceeded as seen in Table 4.

Over time, current shows very slow stabilization. In case of some materials, longer experiments need to be performed in order to obtain stable results. Porous media Hurdis caused increased conductivity of the inlet solution which may be a sign of dissociation of material's functional groups and decomposition of the material.

Unstable desalination results are also connected to:

- inappropriate separator, which plays significant role in proper collection of the product
- too low voltage compared with voltage needed for proper shock propagation
- insufficient contact of membrane and porous media.

As the functional area of the membranes is much larger than the one of II generation unit, pressure driven flow through the media may cause a gap between membrane and

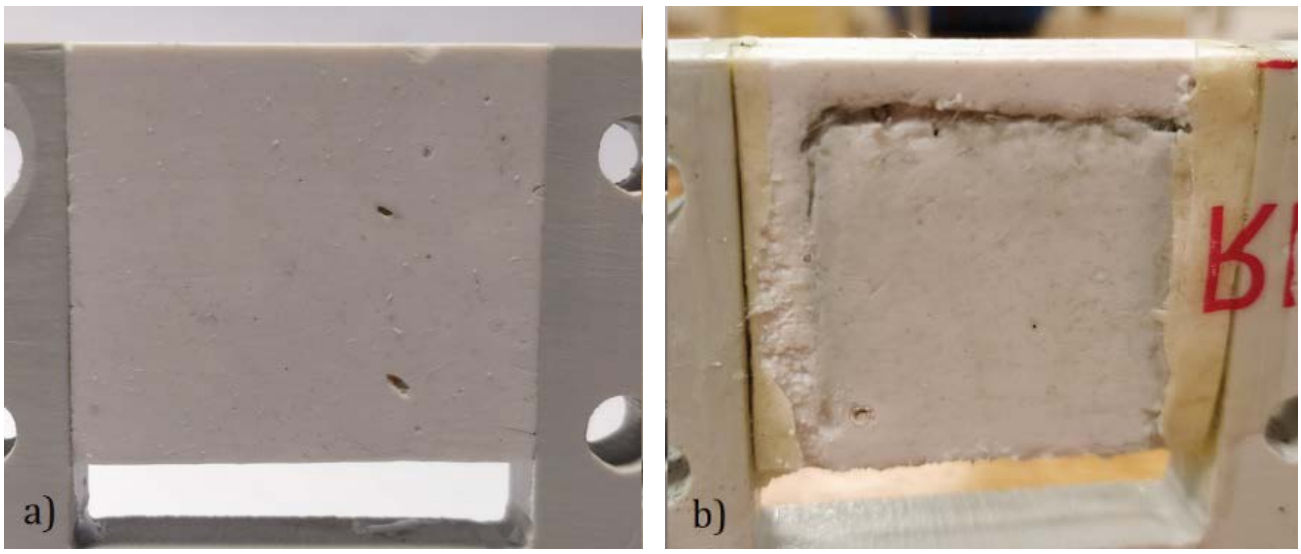

Fig. 6. Fresh (left side) and damaged (right side) porous material (xonolite/tobermorite).

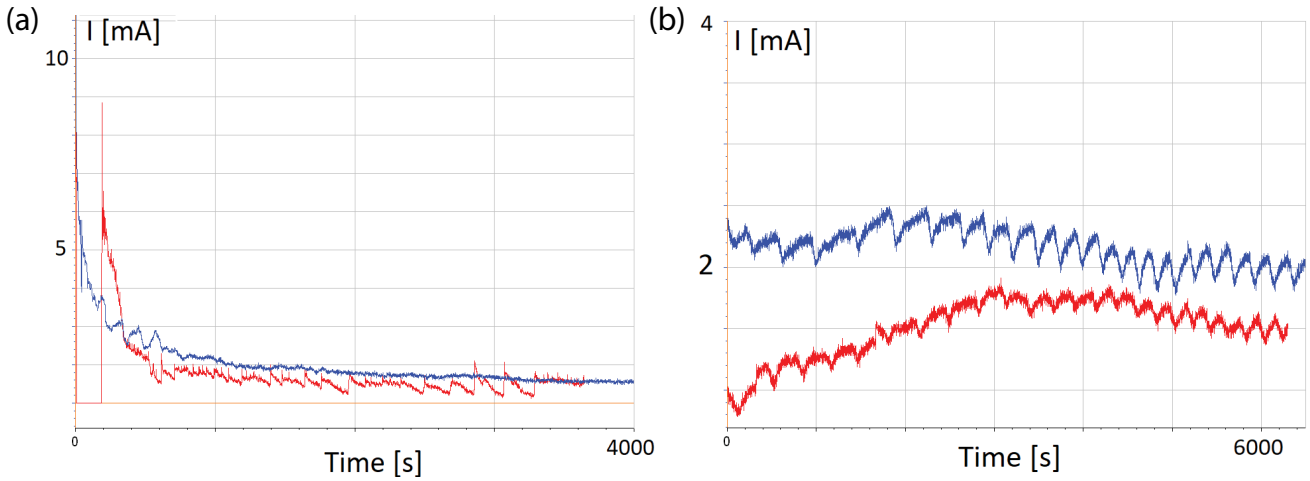

Fig. 7. (a) Chronoamperometry II generation unit and (b) –Chronoamperometry III generation unit.

Table 2
Desalination results for materials applied in II generation shock electrodialysis unit

Material type	Conductivity (mS cm^{-1})		Desalination (%)
	Cathode side outlet	Anode side outlet	
Glass frit	1.4	2.2	36
Porotherm	1.6	2.9	24
Porulit® C530	1.6	2.7	24

media. Surface charge is another quality we were not able to examine, however as all materials contain SiO_2 groups, the negative surface charge was expected. Ideal characterization method for the porous media seems to be device for the measurement of surface tension – zeta sizer (zeta potential).

Table 3
Desalination results over time for III generation unit, tobermorite and xonolite, flow rates: 1 mL min^{-1} inlet, 8 mL min^{-1} catholyte and anolyte

Time of experiment (s)	Outlet side	Conductivity (mS cm^{-1})
0	Reference (inlet)	2.09
1,000	Anode	1.92
	Cathode	1.69
2,000	Anode	2.05
	Cathode	1.78
3,000	Anode	2.11
	Cathode	1.98
4,000	Anode	1.90
	Cathode	2.08

Table 4
Desalination results for III generation unit, Hurdis fired brick, flow rates: 0.3 mL min^{-1} inlet, 0.9 mL min^{-1} catholyte and anolyte

Time of experiment (s)	Outlet side	Conductivity (mS cm^{-1})
0	Reference (inlet)	2.45
1,800	Cathode	2.63
	Anode	4.21
3,300	Cathode	3.00
	Anode	3.91
4,500	Cathode	3.25
	Anode	4.61

4.4. IV generation unit design and future work

Recently, another IV generation SED unit was designed (in collaboration with MemBrain Ltd., Stráž pod Ralskem) based on the current experiences, providing the possibility of scale-up to multiple chambers. This unit houses porous medium with larger size, using standard ion exchange membranes (Ralex CF-R-14, Mega corp., Stráž pod Ralskem) and providing approximately 200 mm length of the inlet path with 200 mm × 100 mm active membrane surface and larger flat electrodes from platinum covered titanium (not mesh). The separator (of diluate and concentrate wave) is built in frame and the outlet is collected just in two streams instead of six outlet points. The contact of the membranes with the porous medium is assured by distance (spacer) plastic mesh filling the anolyte and catholyte chambers.

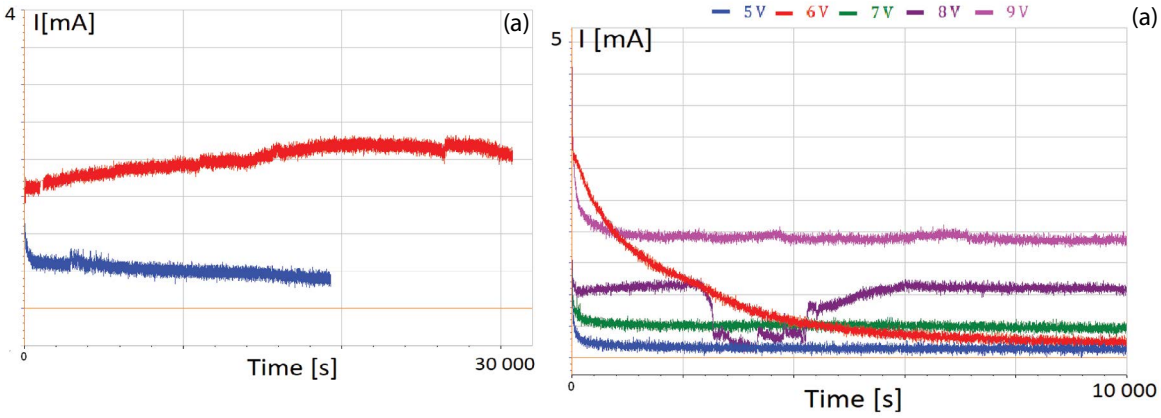

Fig. 8. Chronoamperometry of III generation SED unit, (a) fired brick hurdis and (b) tobermorite & xonolite.

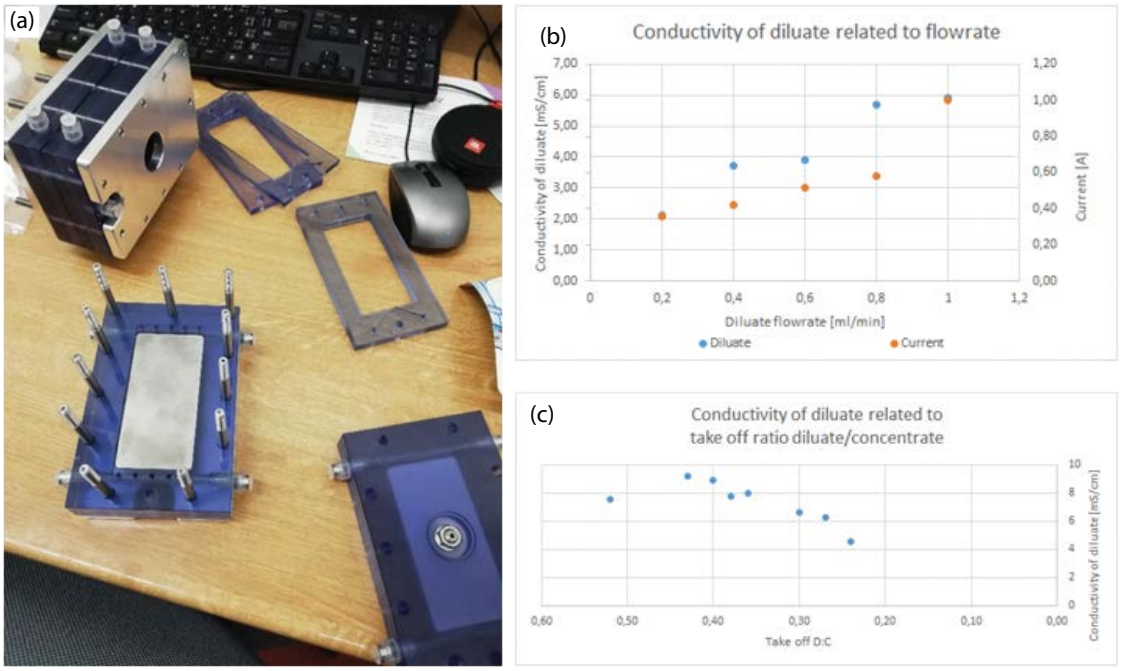

Fig. 9. (a) Shock electrodialysis unit "IV generation" (scalable – multiple chambers). and (b,c) conductivity of diluate related to flowrate and take off ratio diluate/concentrate. Inlet solution is Na_2SO_4 with conductivity 14 mS cm^{-1}. The IV generation 1-chamber unit (1 membrane pair – cat.ex).

This unit has designed more robust, more practical version of the III generation unit for the future scale-up to multiple chambers. The future work includes testing the effects of higher voltages, long-term experiments (more than 70 h) and various types of separators and porous materials, as the housing of the media is easier to change. The results of the early experiments show stable 70%–80% deionization of the inlet solution Na_2SO_4 with 14 mS cm^{-1} conductivity, but the outlet solution, the porous medium and other conditions affecting these results are yet to be characterized.

The data from experimental results in Figs. 9b and c arouse the question of setting suitable parameters for reaching shock wave. The discussion and new experiments are worth new publication which will follow this article.

5. Conclusion

The work shows application of porous media in SED unit. Best results obtained in reference works [10] reached nearly 100% ion removal, which does not correlate with results achieved in this work. Desalination of 36% obtained in this work arouses question of reaching/missing theoretical shock wave in real operation. According to the study by Nikonenko et al. [5] and Zabolotsky et al. [7], there is a limit for width of channels in porous material (10 μm) but this value is not even mentioned at [10]. Our experimental results imply the need for improvement of the design of both the unit and the media in bigger devices. From the unit design point of view, the crucial parts to be optimized are the sealing of the unit, the outlet separator and the inner parts of the unit to ensure the contact of the membranes with the medium. These and other design changes have already been partly applied in the IV Generation unit and will be tested in the future work. Nevertheless, various materials and a wide selection of ceramics can be applied. Porosity of the media should be high enough to allow flow rates within reasonable pressure applied to reach reasonable operation costs on an industrial scale. This is connected to adequate channel size which can still can propagate the shocks. The uniformity of the porosity of the material is still disputable. Surface charge and its density should be characterized ideally by the zeta-potential. The media size (length of inlet path) reflects concentrate and diluate separation. Thickness needs to be adequate for optimal shock propagation while providing sufficient room for sampling. It is possible, that ideal thickness is individual to specific materials and the experiment parameters including the applied voltage. Last but not least is the mechanical stability and workability of the porous material that will play the role particularly in scaling of such system. These parameters need to be properly characterized and optimized for used porous material in order to produce ultrapure water.

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