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Desalination by electret technology

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Abstract

A purification process of making use of electret technology for efficient but cost effective deionization was discussed in this paper. Douglas MacGregor claimed that PTFE electret works as a means of ions separation for desalination due to the polarization of an electrolyte and ions migration under a permanent electrostatic field generated by a pair of electrets with opposite polarities. The electrostatic field attracts counter-ions to the charged solid surface, and thus generates a purified effluent in the mainstream. Theoretical and experimental analyses were made to investigate the practicality of desalination by electret technology. It is found that MacGregor's design is meaningful only for a dilute electrolyte or a system with very high surface charge density because the number of the counter-ions attracted to the surface is limited and cannot exceed that of the surface charges at the electret.

Keywords: Desalination; Electrets; Potential; Ions density; Ion chromatography

1. Introduction

Desalination by electret technology (DET) was introduced by Douglas MacGregor in his two patents [1,2], which make use of a permanent electrostatic field generated by a pair of PTFE electret sheets with opposite polarities for ions separation. Under such electrostatic field, the anions, cations and electric dipoles in an electrolyte will be drifted out of the mainstream to side channels due to electrostatic interactions and thus leave the mainstream free of ions when the electrolyte to be processed flows through the tube separated by two pieces of membranes as described in MacGregor's cylinder design.

Unlike capacitive deionization [3,4] (CDI), a process which relies on the sorption capacity of polarized materials (carbon aerogel) too, the reason of using a polarized material in DET is to make use of its permanent electrostatic property. Moreover, DET has further differences than CDI as follows:

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- Simplified apparatus with low cost and easily manufactured polarized material.
- No electricity used and no conductive material such as carbon aerogels, therefore metal ions are not neutralized as would be the case in CDI.
- Mobile ions in the diffusion layer of electric double layer (EDL) [5–7] stay in the side channel always, not included in the output purified effluent.
- Membranes are used as mechanical barriers which discourage the ions from remixing in the neutral mainstream.

To other current desalting techniques [2], utilization of permanently polarized materials not requiring continuous energy input other than pumping the liquid moving through the system [2], no chemical or secondary waste produced, and the striking purification result (>99.0%) claimed in MacGregpor's patents, all of these might have indicated that DET will be an efficient but cost effective way of providing purified potable water. Before commercializing the DET technology, US Bureau of Reclamation funded to assure the practicality of MacGregor's patents.

In this article, experimental results of applying electret technology to low-cost desalination were generalized to investigate the idea's correctness and the possibility of commercializing the DET technique, together with the theoretical fundamentals behind the potential distribution and ions movement in the electrolyte under a permanent electrostatic field produced by electret.

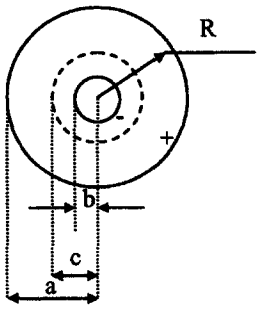
2. Theoretical analyses

The cylinder design employed by MacGregor is given in Fig. 1a. The outer tubular member that is of hollow construction of radius a is positively charged, and the inner solid rod of radius b is negatively charged. These two members are PTFE electrets with the same charge density of σ but opposite polarities. The boundary conditions in this configuration are given by Eq. (1),

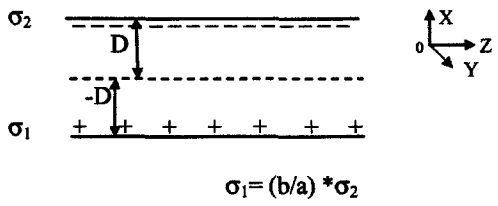
$$\begin{aligned} d\psi/dr &= -4\pi\sigma/\varepsilon_o\varepsilon_r \quad \text{at } r=b \\ d\psi/dr &= 4\pi\sigma b/(\varepsilon_o\varepsilon_r a) \quad \text{at } r=a \\ \psi_c &= 0 \quad \text{at } r=c \end{aligned} \tag{1}$$

where r is the radial distance, ψ is the potential at any r, ε_o is the permittivity of a vacuum; ε_r is the dielectric constant of the solution.

As stated, the purification effect of DET technology depends on the permanent electrostatic field generated by the electret with opposite polarities, but not the cylinder configuration. A planar system would achieve the same desalination goal as cylinder design does. On the other hand, the boundary conditions in the planar design shown in Fig. 1b are



(a) Circular Design



(b) Planar Design

Fig. 1. Cross-area of the channel systems.

$$\begin{aligned} d\psi/dx &= -4\pi\sigma_2/\varepsilon_o\varepsilon_r \quad \text{at } x=-D \\ d\psi/dx &= 4\pi\sigma_2 b/(\varepsilon_o\varepsilon_r a) \quad \text{at } x=D \\ \psi_c &= 0 \quad \text{at } x \approx D(b-a)/(a+b) \end{aligned} \tag{2}$$

which implies that planar design has the similar potential distribution as in a cylinder design. It is thus reasonable to replace the circular design by a planar design to simplify the theoretical analysis next.

As a PTFE electret is in contact with a NaCl electrolyte, ions which have opposite electric sign to the polarity of the electret employed will be attracted to the area adjacent to the corresponding PTFE charged surface in the electrolyte solution. This, together with the mixing tendency of thermal agitation, leads to the formation of an electric double layer (EDL) made up of a Stern layer and a neutralizing excess of counter-ions over co-ions distributed in a diffuse layer in the polar medium [6–11]. EDL behaves like an electric capacitor, and there is a potential drop [5] across the EDL. A restricted primitive model (RPM) [12,13] of a symmetric 1-1 electrolyte is used for theoretical analyses. In a RPM, the ions are represented by charged hard spheres of the same diameter d, and the solvent is treated as a uniform dielectric continuum. In the planar design, the electrolyte is confined between two parallel, semi-infinite planar electret sheets of opposite electric signs located at $x = -D$ and $x = D$ with surface charges density σ_1 and σ_2 respectively ($\sigma_1 < \sigma_2$, Fig. 1b). The ionic densities and the mean electrostatic potential change only with the distance to the charged solid surface due to the planar symmetry configuration. Thus, the electrostatic potential $\psi(x)$ in the diffuse layer is given by one-dimensional Poisson–Boltzmann [13–16] equation:

$$\begin{aligned} &d^2\psi/dx^2 \\ &= (-1/\varepsilon_o\varepsilon_r)\sum n_i^0 z_i e \exp(-z_i e\psi/KT) \end{aligned} \tag{3}$$

where, n_i^o is the numbers of ions of type i per unit volume in the bulk solution far from the surface, z_i is the valency of electrolyte ions of type i, e is the elemental charge, K is the Boltzmann constant, and T is the temperature in Kelvin.

For a symmetric 1-1 electrolyte, the net charge density in Eq. (3) is given by the Boltzmann equation as [16]:

$$\begin{aligned} \rho &= \sum n_i^o z_i e \exp(-z_i e\psi/KT) \\ &= -2n^o e \sinh(e\psi/KT) \end{aligned} \tag{4}$$

where n^o is the bulk ionic concentration. Substituting Eq. (4) into Eq. (3) yields:

$$d^2\psi/dx^2 = (2/\varepsilon_o\varepsilon_r)n^o e \sinh(e\psi/KT) \tag{5}$$

Assuming $e\psi/KT<1$, Debye-Hückel approximation in Eq. (6)

$$\exp(e\psi/KT) \approx 1 + e\psi/KT \tag{6}$$

could be applied to simplify Eq. (5)

$$\begin{aligned} d^2\psi/dx^2 &= \kappa^2\psi \\ \kappa &= \left(2n^o e^2/\varepsilon_o\varepsilon_r KT\right)^{0.5} \end{aligned} \tag{7}$$

At room temperature, 298K, the Debye–Hückel parameter κ is equal to $3.288(n^o)^{0.5}$ nm^{-1}. In an electrolyte, the ions cannot reach up to the charged surface because of their finite size (Fig.2), so there is a charge-free region right near the electret. The system satisfies:

$$\begin{aligned} \psi(d/2)^+ &= \zeta_1 \quad \text{at } x = -D + d/2 \\ \psi(d/2)^- &= \zeta_2 \quad \text{at } x = D - d/2 \\ \psi &= 0 \quad \text{at } x = (\sigma_2 - \sigma_1)D/(\sigma_1 + \sigma_2) \end{aligned} \tag{8}$$

where, $\psi(d/2)$ is the diffuse layer potential, d is the diameter of ions. Let ψ_o be the surface potential,

$$\psi_0 = \psi(d/2) + 2d\pi\sigma/\varepsilon_o\varepsilon_r \tag{9}$$

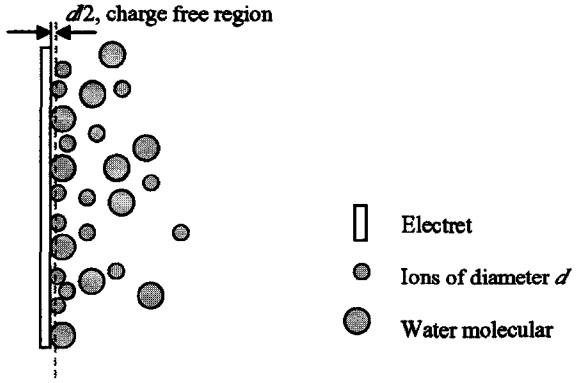


Fig. 2. Particles distribution near a charged surface.

In terms of MacGregor's claim, the surface charge density of the electrets used for desalination is only 1.268×10^{-6} coul/m^2. Zixiang Tang et al. [17] give the relationship between diffuse layer potential and surface charge density for a 1-1 electrolyte. The diffuse layer potential for MacGregor's configuration is much less than 25.68 mV. Hunter [18] states that the Debye–Hückel approximation is valid when $\psi(d/2)$ is less than about 25 mV at room temperature. Therefore, the simplification we made to Eq. (5) is valid. Applying the boundary conditions in Eq. (8) to Eq. (7) yields:

$$\psi_1(x)=\zeta_1\frac{\left|\sinh\left[\kappa\cdot\left[x-D\cdot\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)}\right]\right]\right|}{\sinh\left[\kappa\cdot\left(D-\frac{d}{2}\right)-D\cdot\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)}\right]}\qquad x<D\cdot\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)} \tag{10-1}$$

$$\psi_2(x)=\zeta_2\cdot\frac{\left|\sinh\left[\kappa\cdot\left[x-D\cdot\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)}\right]\right]\right|}{\sinh\left[\kappa\cdot\left(D-\frac{d}{2}\right)-D\cdot\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)}\right]}\qquad x>D\cdot\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)} \tag{10-2}$$

According to Boltzmann equation,

$$n_i=n_i^o\exp\left[-z_i e\psi/(KT)\right] \tag{11}$$

here n_i is the respective numbers of ions of type i per unit volume at positions where the potential is ψ.

The number of counter-ions attracted to the surface from the mainstream is:

$$N_{extra}=\int_{D\frac{(\sigma_2-\sigma_1)}{(\sigma_1+\sigma_2)}}^{-D+\frac{d}{\epsilon}}\left(n^o\right)_i\cdot\exp\left[-z_i e\cdot\psi_1\frac{(x)}{KT}\right]dx-\left(n^o\right)_i\left[(\sigma_2-\sigma_1)\cdot\frac{D}{(\sigma_1+\sigma_2)}\right] \tag{12}$$

The number of attracted counter-ions is related to the charge density of the electret. It cannot exceed the surface charges on the polarized materials, since the electric field generated by the surface charges would be offset by the accumulated counter-ions, which would cause that there is no ion movement anymore.

The purification efficiency by DET is decided by how many counter-ions passing into the side region from the mainstream. The field strength stated in Macgregor's claim is 18,000 V/cm which gives that the charge density of the PTFE electret is at magnitude of 10^{10} per cm^2, that is much fewer than the ions density (10^{19} per cm^3) in the input mainstream of 3 wt% sodium chloride solution. The theoretical analyses indicate that the number of the counter-ions attracted to the area near the electret is limited, and no more than the number of surface charges on the electret. It is not logical to have 5.2 ppm diluted effluent. Experiments were thus simulated to verify the desalination results by DET process.

3. Experiments and discussion

The electric field was measured by Monroe Model 257 electrostatic fieldmeter with accuracy of 5%, and the concentration and conductivity of the sodium chloride solution was given by a Horiba Conductivity Meter ES-14 with conductivity reproducibility of ±0.5%. Corona-treated polypropylene electrets manufactured by *CLINGZ* Permacharge Corporation, New Mexico, functioning as PTFE electret, were used to generate the permanent electrostatic field, as Fig. 1b shows. The inner surfaces of the two polypropylene sheets (0.005 inch thick) were of opposite polarities.

Conductivity represents the total ion concentration in an electrolyte. Experiments [19] verified that the ion concentration is proportional to the conductivity of the electrolyte, especially at high concentration range (>1%wt). In this article, conductivity of the solution was measured rather than the concentration. A planar configuration instead of circular one was used for verification purpose. The edges of each electret sheet were sealed and kept the back side dry to prevent the generated electric field from being destroyed [5, 19]. A sodium chloride solution slab was enclosed by two pieces of polypropylene sheets with opposite polarities, one having external measured electric field of 5.5 kV/cm, and the other of −18.6 kV/cm.

3.1. Ion chromatography

Ion chromatography was investigated by a 5-layer model shown in Fig. 3. A Teflon separator is employed to form a solution channel (length: 254.0±0.5 cm, width: 1.0±0.05 cm, height: 0.157±0.05 cm. Highly purified water (pH 7.0, 0.89 us/cm, produced by Department of Chemistry at DU) was first pumped through the solution channel for 10 min. 1 ml saline-rich slug of water was then injected into the input stream by a calibrated syringe. The conductivity of the effluent stream was measured continuously and recorded by a Pentium computer installed with LabView software.

Ions, electric dipoles, and suspended particles were dispersed by the velocity gradients (Poiseuille flow) [20]. Besides these immobile counter-ions attracted to the Helmholtz layer [3], because of strong electrostatic interaction between ion-wall,

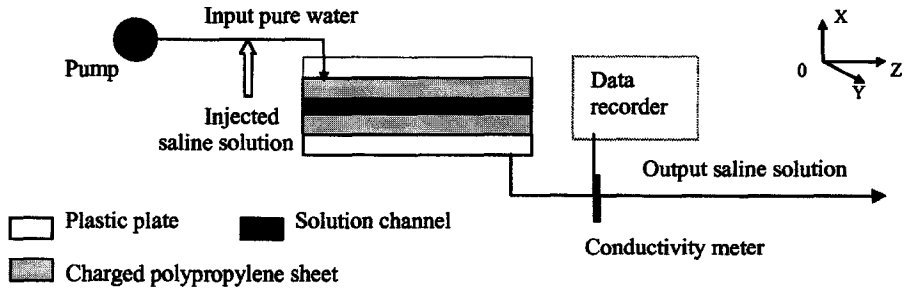


Fig. 3. 5-layer DET purification model.

the channel adsorption contributes somewhat to deionization too. An elution test without membrane separation was carried out to investigate ions removal due to surface adsorption to the channel components (electret sheets and Teflon separator). The channel was cleaned by immersed into pure water after every test, together with fresh electret sheets changed.

3.1.1. Flow rate effect

Three different flow rates, 0.46±0.02 ml/s, 0.87±0.02 ml/s, and 1.21±0.02 ml/s, supplied by a Masterflex® tubing pump, were processed to study the flow rate effect. The concentration of the injected saline solution was 1.931±0.01 wt%. The laminar flow transport in a rectangular cross section shown in Fig. 3 is described below [20]

$$Q = qB^3 W \Delta P / (3\eta L) \tag{13}$$

$$V_z = B^2 \left(1 - x^2 / B^2\right) \Delta P / (2\eta L) \tag{14}$$

here, Q is the volume flow rate Q and V_z is the flow velocity in Z direction, L is the channel length, $2B$ is the thickness of the channel, W is the width of the channel, ΔP is the pressure drop over the channel, and h is the viscosity of the solution.

Non-ideal retention time distribution (RTD) curves for ions chromatography were plotted in Fig. 4. The interferences from turbulence-like instabilities, such as flowing pattern changed by injected fluid and rough channel surface, made the RTD curve more uniform for higher flow rates. The higher the flow rate, the sooner the RTD peaks observed. An enclosed area of any RTD curve in Fig. 4 represents the amount of ions flowing out. It is shown that the number of saline ions left in the channel was proportionally upon the flow rate. According to Eq. (14), the flow velocity gets the maximum value at the middle plane of $x = 0$. For a liquid at a flow rate of 0.46 ml/s, the maximum flow velocity in the rectangular channel was

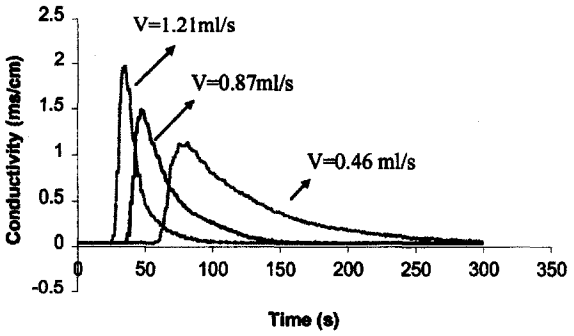


Fig. 4. RTD at different flow rates.

4.395 cm/s, so the injected saline ions was supposed to arrive at another end in 57.8 s, about 3 s less than the measured time showed in Fig. 4. The time difference here might be caused by the flow resistance resulting from the macro-rough surface of the Teflon channel.

3.1.2. Concentration effect

Two different saline solutions of 1.19±0.01% and 1.93±0.01% were injected into pure water respectively as described above to study the concentration effect on ions chromatography. The flow rate employed was constant at 0.87±0.02 m/s. The experiment results were given in Fig. 5.

The two experimental RTD curves exhibited are similar. The very first times of observing the saline ions and RTD peak in the output effluent are independent of the salt concentration of the injected fluid. At a fixed flow rate, the mobile ions

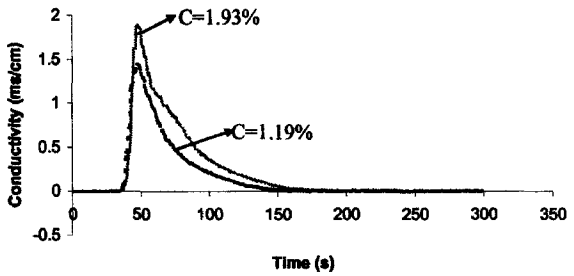


Fig. 5. RTD at different concentrations.

in the solution showed the same behavior of movement along the channel under a fixed electric field, while more surface adsorption to the channel was happened to the effluent injected with denser saline solution.

3.3.3. Effect of Helmholtz layer

The corona-treated polypropylene sheets were replaced by uncharged ones in the 5-layer model to check if there is any ions adsorption to the Helmholtz layer near the electret surface under an electrical field. The results are given in Fig. 6. The concentration of the injected NaCl solution was 0.143±0.01 wt%, and the flow rate was 0.87±0.02 ml/s.

The electric field resulted from the charges on the electret accelerated the ions movement along the channel even the field was perpendicular to the flow direction, which has been shown by the inconsistence of the appearance of the RTD peak compared with that with uncharged polypropylene sheet. There were a little fewer saline ions in the output fluid for the system with charged polypropylene sheets based on the area analysis made to the RTD curves in Fig. 6,. Generally, the surface adsorption, no matter adherence to the channel or attracted to the electret surface by electrostatic interactions, exists absolutely in the system developed here. The problem is that the amount absorbed is too small to give much contribution to the desalination as MacGregor claimed. So, membrane was used next as a mechanical barrier

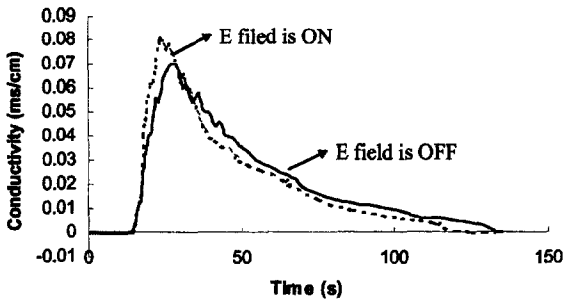


Fig. 6. Effect of an electric field on elution.

to separate the ions which are in the diffusion layer of an EDL from the main stream.

3.2. Desalination

The desalination configuration employed here was the same as that described in ion chromatography, except three Teflon channels plates rather than one plate were used, which were separated by a couple of Millipore membranes containing 3~5 um pores. The membranes employed discourage the ions attracted from remixing in the mainstream [1]. And thus the output effluent was divided into one mainstream and two side-stream effluents. Several kinds of NaCl electrolytes with different saline concentrations (given in Table 1) were pumped through the channel, and the flow rate was 1.21±0.02 ml/s. Three experiments were done for each concentration. Every time, before different NaCl solution would be processed, the system was cleared by pure water, and had the electret sheets and membranes

Table 1
Desalination results, wt %

Input		Mainstream	Mixed side-stream	Reduction (%)
Concentration (wt %)	Conductivity (ms/cm)	Conductivity (ms/cm)	Conductivity (ms/cm)	
2.98	52.81	51.87±0.67	52.92±0.62	1.78
2.10	31.56	31.11±0.48	31.60±0.51	1.43
1.21	19.45	19.09±0.24	19.63±0.36	1.85
0.53	9.40	9.19±0.13	9.47±0.11	2.23
0.09	1.07	1.05±0.01	1.06±0.01	1.87

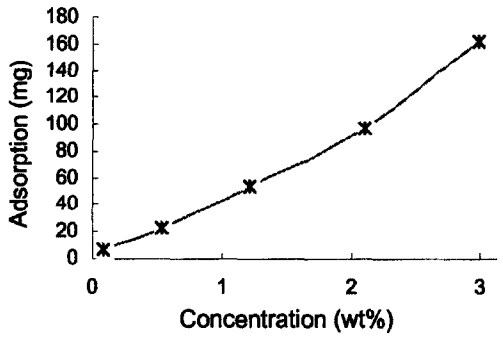


Fig. 7. Replaced membrane gains weight after desalination run.

replaced by fresh ones. A relatively diluted solution was to be expected from the mainstream output, and the enriched solutionwais expected by mixing the two side-stream outputs. The experiment results are listed in Table 1.

The maximum reduction achieved is only 2.23%, much less than what Macgregor claimed. And much salt absorbed to the replaced membrane, which was verified by measuring the weight different to the original membrane and after-service dry replaced membrane (Fig. 7). Based on the theoretical analysis made in part II, the ratio of ions adsorbed to EDL is much less than 0.1%. The major reductions got in the simulation experiments mainly come from membrane adsorption. The reduction ratio obtained was also not encouraging even we changed the configuration, such as changing the surface charge density of the electret, narrowing the channel size, etc.

4. Conclusion

The mean electrostatic potential $\psi(x)$, influenced by both the surface charges and the ionic charges in the electrolyte, cannot be infinite. In other words, the reversal electric field produced by the ionic charges in the electrolyte is always less than the external field generated by the surface charges on the electret employed. The number of the counter-ions attracted to the surface cannot exceed the surface charges on the polarized materials; otherwise, the electric fields across the solution will reversely repel these counter-ions far away to the bulk.

In DET, counter-ions are attracted to the area adjacent to the opposite-charged electret surface by the external electrostatic field, and the membranes utilized as mechanical barriers prevent ions from remixing in the neutral mainstream. Experiments of applying DET technology to NaCl electrolytes in the general manner prescribed in Douglas MacGregor's patents were done, but little significant separation was observed, and membrane adsorption played an important role in our observation. Unfortunately, MacGregor's claim is only valid for a very dilute saline solution or an electret with a very high surface charge density, at least at magnitude of 10^3 coul/m^2 that could not be achievable currently. However, the concept of using electret for desalination is considered to be viable and should be developed further.

Acknowledgement

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References

[1] D. MacGregor, Method and Apparatus for Separating Ions from Liquids to Produces Separate Diluted and Concentrated Effluents, US Patent 4,948,514, 1990.
[2] D. MacGregor, Method of Separating Ions from Liquids, US Patent No. 5,061,376, 1991.
[3] J. Farmer, Method and Apparatus for Capacitive Deionization, Electrochemical Purification and Regeneration of Electrode, US Patent 5,425,859, 1995.
[4] J. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala and J.F. Poco, J. Electrochem.Soc.,143 (1996) 159.

[5] H. Ni and R. Amme, J. Colloid Interface Sci., 260(2) (2003) 344.
[6] D.J. Shaw, Introduction to Colloid and Surface Chemistry, Butterworth-Heinemann Ltd., Oxford, 1989.
[7] R.J. Hunter, Introduction to Modern Colloid Science, Oxford University Press, 1993.
[8] L. Zhang and H.T. Davis, J. Chem. Phys., 98(7) (1993) 5793.
[9] A. Braslau, P.S. Pershan and G. Swislow, Phys. Rev. A, 38 (1988) 2457.
[10] J. Penfold, Progr. Colloid. Polym. Sci., 81 (1990) 198.
[11] R. Moberg, F. Bökman and O. Bohman, J. Chem. Phys., 94(7) (1991) 5226.
[12] C.N. Patra and S.K. Ghosh, Phys. Rev. F, 47 (1993) 4088.
[13] Z. Tang, L.E. Scriven and H.T. Davis, J. Chem. Phys., 97(12) (1992) 9258.
[14] D. Henderson and P. Bryk, Phys. Rev. E, 61(4) (2000) 3896.
[15] P. Attard, D. Wei and G.N. Patey, J. Chem. Phys., 96(5) (1992) 3767.
[16] D. Erickson and D. Li, J. Colloid Interf. Sci., 232 (2000) 186.
[17] Z. Tang, L.E. Scriven and H.T. Davis, J. Chem. Phys., 97(1) (1992) 494.
[18] R.J. Hunter, Zeta Potential in Colloid Science, Principles and Applications, Academic Press, NY, 1981.
[19] R. Amme and H. Ni, Desalination Research and Development Program Report No. 73. US Department of the Interior, Bureau of Reclamation, 2002.
[20] W.J. Beek and K.M. Muttzall, Transport Phenomena. J. Wiley and Sons, NY, 1975.