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Capacitive deionization of water using mosaic membrane

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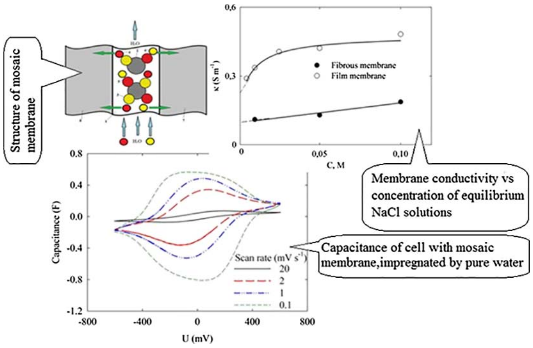
GRAPHICAL ABSTRACT



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ABSTRACT

Capacitive deionization of water using membrane-electrode assembly was researched. The approach that allows to decrease energy consumptions of water purification was considered. The method provides usage of mosaic membrane containing both cation and anion exchange fragments instead of glass spacer. Counter-ions inside the membrane ensure rather high ionic conductivity even in pure water. Mosaic membranes based on polyethylene (film type) and phenol-formaldehyde (fibrous type) matrices were studied, their electric conductivity and exchange capacity were determined. Deionization in static and dynamic electrochemical cells, which were filled with deionized water and 0.005 M KCl solution respectively, was researched. The mechanism of electric double layer charging inside pores of the electrodes impregnated with pure water has been proposed. Specific energy consumptions for deionization of very diluted solutions are sufficiently lower for the cell containing mosaic membrane than those for the cell with inert glass spacer. Minimum energy consumptions and maximum deionization degree are reached at cell voltage of 1.4 V. The value of specific energy consumptions is 12 Wh mol^{-1} for the laboratory cell containing the mosaic membrane, when degree of deionization reaches 50%, cell voltage is 1.4 V, electrode area is 50 cm^2, initial concentration of the KCl solution is 0.005 M.

Abbreviations: AC, activated carbon; CDI, capacitive deionization; ECSC, electrochemical supercapacitor; EDI, electrodeionization; EDL, electric double layer; HDCE, highly dispersive carbon electrode; MCDI, membrane capacitive deionization; MEA, membrane-electrode assembly; MM, mosaic membrane; MSCP, method of standard contact porosimetry

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1. Introduction

Capacitive deionization (CDI) is a promising electrochemical method of water desalination. Economically, it is the most attractive technique in comparison with reverse osmosis (3 times cheaper) [1,2], distillation, and electromembrane separation due to lower energy consumptions [1–3] and simpler equipment [4]. As opposed to electrodeionization (EDI), which involves ion exchange membranes and granulated polymer [5–7] or inorganic [7] ion-exchanger between them, electrodes play the key role in CDI processes. CDI involves the passage of aqueous solution through the electrochemical cell between two highly dispersive carbon electrodes (HDCEs) with high specific surface area (500–2500 $m^2 g^{-1}$) [1,2,8]. Low potential difference (≥ 1.2 V) is applied providing a high safety level. Porous inert spacer is placed between the electrodes to separate them. In a number of works, for instance in [9], glass or polymer fibrous plate is used as a spacer.

Adsorption of anions and cations occurs on positively and negatively charged electrodes respectively, electric double layer (EDL) is charged similarly to that in an electrochemical supercapacitor (ECSC) [10,11]. This results in deionization of the solution. When the circuit is closed or polarity is reversed, ions diffuse from the solid-liquid interface back to the solution, increasing the solution concentration and causing energy regeneration. The deionization stage corresponds to the charging of the ECSC, while the regeneration stage is related to discharging. During the regeneration stage, significantly lower amount of water is supplied to the cell. After regeneration of the electrodes, the cell is converted to a deionization cell, whereas CDI device including at least two electrochemical cells operates continuously. In other words, while deionization takes place in the first cell, regeneration occurs in the second cell. Thus, the consumed energy can be partially compensated by electrical energy from the regeneration unit.

Electrode materials for CDI have been in the focus of attention in the last years. Different types of both single-component, such as activated carbon (AC), aerogels, nanotubes, graphene [12–15], and AC–based composite materials (AC-AC composite, AC-metal oxide composite, AC-polymer composite and AC-polymer-metal oxide composite) [16–19] have been suggested. CDI application for removal of different salts from water has been investigated in detail [20–22].

In [23,24]., the equations predicting the lowest regeneration time and the highest desalination degree for CDI at constant current have been found using the mathematical model of adsorption cycle. During purification process, the effluent concentration reaches the highest purity level after a certain period of time.

The method of membrane capacitive deionization (MCDI) can be considered as a modification of CDI. In this case, the anion exchange membrane is adjacent to the positively charged electrode, and the cation exchange membrane borders on the cathode [25–28]. The anion exchange membrane prevents cation transport to the anode, while the cation exchange membrane makes impossible anion movement towards the cathode. This provides more complete separation of cations and anions in the MCDI cell. When the HCDEs, which are characterized by high specific surface area, are used and no membranes are applied to the CDI process, separation of oppositely charged ions occurs due to EDL charging inside pores of the electrodes. However, the membranes provide additional hydrodynamic resistance (increasing energy consumptions). This is a disadvantage of the MCDI method in comparison with CDI.

Deep water purification requires high energy consumptions also in the case of CDI because of high ohmic losses caused by huge electrical resistance of pure water. At the same time, ionic conductivity of AC electrodes is rather high even in pure water [29] due to surface conductivity caused by large amount of ion exchange groups on the surface of carbon materials [30]. Therefore, at the final stage of the deionization process, energy consumptions are determined by practically zero conductivity of water, which fills pores of the spacer between the electrodes.

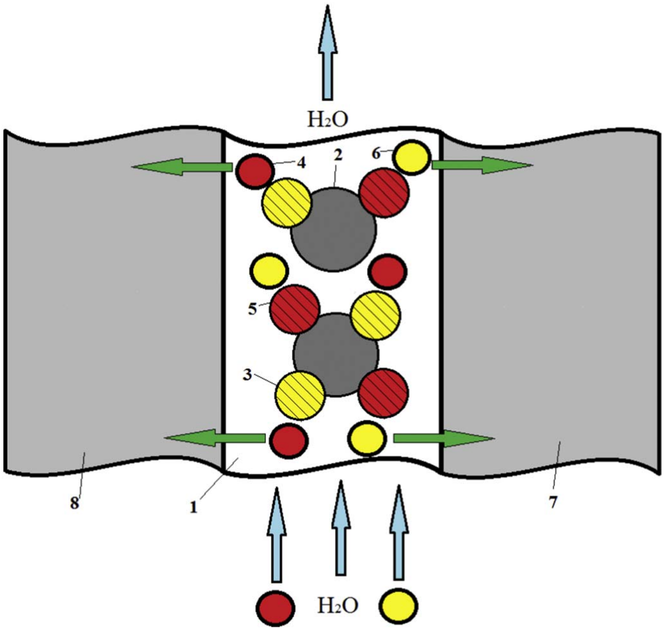

Fig. 1. Structure of MM: 1 - polymer matrix (polystyrene matrix cross linked with divinylbenzene for film type of mosaic membrane or phenol formaldehyde for fibre type of mosaic membrane); 2 - micropores and mesopores; 3 - positively charged fixed groups (amino groups) in anion-exchanger particles; 4 - anions (counter-ions to anion-exchanger); 5 - negatively charged fixed groups (sulfo groups) in cation-exchanger particles; 6 - cations (counter-ions to cation-exchanger); 7 - cathode; 8 - anode.

The aim of the work was to develop and investigate the membrane-electrode assembly (MEA) for CDI processes to obtain pure water. The MEA design provides specially manufactured membrane of mosaic structure (mosaic membrane, MM) instead of inert porous spacer in order to decrease energy consumptions as much as possible. The membrane contains both cation and anion exchange groups. It is also necessary to use HDCEs that are characterized by highly developed surface and contain oppositely charged surface groups. As assumed, the energy losses for the MEA are much less than those for the cell containing a conventional porous spacer. This is due to high ionic conductivity of MM that is caused by ion exchange groups (similarly to any ion exchange membrane).

2. Experimental

2.1. Membranes

Mosaic membranes (MM), in which cation- and anion exchange fragments are randomly and homogeneously distributed through the volume of inert polymer matrix (Fig. 1), were applied to investigations. In fact, the whole volume of this membrane is characterized by mosaic structure. According to the review [31], similar membranes are related to amphoteric materials, As for known MM, their cation and anion exchange fragments are continuous and located in parallel to each other. Thus, each fragment provides continuous pathway for ion transport. However, mosaic structure is attributed only to outer surface of the membrane, not to the whole volume.

Both film and fibrous MM were used in this work. The film heterogeneous membrane produced by NIIPM Company (Engels, Russia) was manufactured by mixing of powders of AV-17 anion exchange resin (70 mass %) and KU-2 cation exchanger (30%). The resins were produced by Schekinoazot Company (Schekino, Russia). Polyethylene was used as a binder, nylon threads were also applied in order to provide mechanical durability of the membrane. The mixture was formed into sheets under elevated pressure and temperature [32]. Structure and functional properties of MM of different composition were investigated