



*V.I. Vernadskii Institute  
of General and Inorganic Chemistry  
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# **MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE**



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**CHAPTER 15****CAPACITIVE DEIONIZATION OF WATER (REVIEW)**

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**Abstract.** *The method of capacitive deionization of water (CDI) is to pump brackish water or seawater through an electrochemical cell, where certain potential difference is kept between carbon electrodes, which are characterized by high specific surface area. This method is sufficiently more attractive from the economical point of view in comparison with other desalination techniques, particularly with reverse osmosis that is widely used in industry. Different modifications of CDI have been developed, for instance, membrane capacitive deionization of water (MCDI) with cation and anion exchange membranes, CDI with ion-selective carbon electrodes, CDI with flow electrodes, CDI with Na-intercalating electrodes, CDI with cation-exchange and anion exchange mixed membrane of mosaic structure, which is used instead of conventional porous separator.*

**Keywords:** *capacitive deionization, mosaic membrane, carbon electrode, Na-intercalating electrode, membrane capacitive deionization.*

**Introduction.** Capacitive deionization of water (CDI) is an effective new method for desalination of brackish water [1]. Its stream flows between pairs of carbon electrodes, which are characterized by high surface area (HSACE). For example, activated carbon electrodes (ACE) are applied to CDI processes, the electrodes are kept at a potential difference of  $> 1.2$  V. Ions and other charged species are attracted to the opposite charged electrode, which keeps them. The negative electrode adsorbs cations, while the positive electrode adsorbs anions. Eventually the electrodes become saturated with ions and must be regenerated. When the electrical circuit is opened, ions are removed from the electrodes producing more concentrated brine stream. In practice, CDI processes produce deionized potable water and concentrated brine solution, the ratio of their volumes is 4:1. The concentrate contains all salts, which were present in the feeding solution. The main advantage of CDI is low operating cost, this is three times less comparing with the main competitor – reverse osmosis. The mechanism of the CDI processes is based on charging - discharging of electric double layer (EDL) similarly to EDL of supercapacitor.

**Results and discussion.** Different modifications of CDI processes are known, for instance, the method of membrane capacitive deionization (MCDI) [2]. In this case, the anion exchange membrane is adjacent to the positively charged

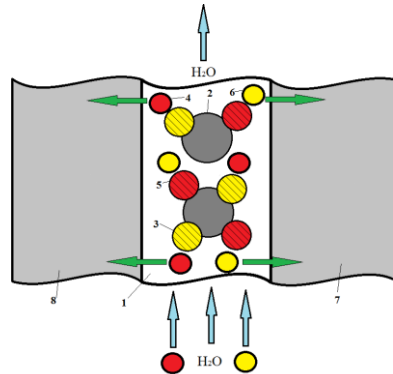
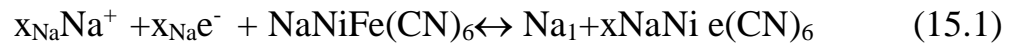
electrode, and the cation exchange membrane borders on the cathode [Fig. 1]. The anion exchange membrane prevents cation transport to the anode, while the cation exchange membrane makes impossible anion movement towards the cathode. This provides more complete separation of cations and anions in the MCDI cell. When the HSACE, 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.

Nitrate-selective composite carbon electrodes (NSCCEs) were manufactured for capacitive deionization to remove nitrate ions selectively from the solution containing different anions. The NSCCEs were fabricated by coating the surface of the carbon electrode with BHP 55 anion exchange resin, this sorbent is known to be selective towards nitrate ions. The resin was ground to a fine powder. The mixed solution containing 5.0 mM NaCl and 2.0 mM NaNO<sub>3</sub> was applied to desalination process using the NSCCE system that involved the fabricated electrode. Selective removal of nitrate ions using the NSCCE and MCDI systems (the last one involved ion exchange membranes and carbon electrodes) was performed, the results have been compared. In the case of the NSCCE system, adsorption of nitrate ions was 19 mmol/m<sup>2</sup>, This is 2.3-times higher than adsorption in the MCDI system. These results showed that ions were initially adsorbed due to electrostatic force, then the species from the solution are sorbed by resin particles of the surface according to ion exchange mechanism.

Another modification of CDI is flow-electrode capacitive deionization (FCDI)[3]. FCDI is novel technology that exhibits continuous deionization and high efficiency ion removal. The flow-electrode possess high capacitance and low resistance, this is necessary to achieve low energy consumptions. In order to develop high-performance flow-electrode, its constituents, such as porous solids, conductive additives and electrolyte, have to be considered. Desalting performances of flow-electrodes containing spherical activated carbon and aqueous electrolyte (NaCl solution of various concentration) has been confirmed (Figure 15.1), the effect of salt concentration in the feeding solution has been found. It has been shown that moderate amount of the salt in the flow-electrode is necessary in order to compensate reduced productivity of the flow-electrode, attributed to decrease of water resistance.

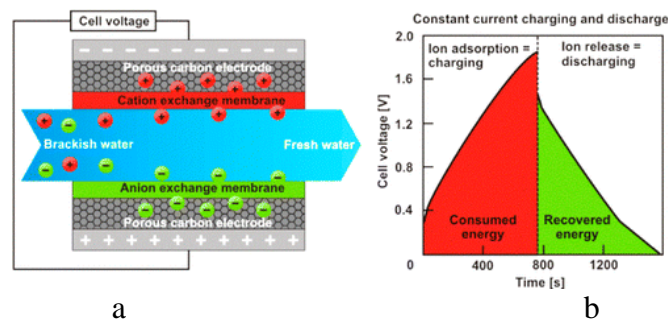
Interesting modification of CDI is membrane-free cation intercalation desalination (CIDI) [4]. In this case, the electrochemical desalination devices involve redox-active cation intercalation electrodes. The stacks are prospective for desalination of salty water, they show high water recovery and low energy consumption. Previous modeling and experiments, which involve ion-exchange membranes to maximize charge efficiency, show rather low capital cost of the processes. At the same time, CIDI (membrane-free alternative) allows us to

reduce the capital cost even more. Porous diaphragm was used to separate  $\text{NaNiFe}(\text{CN})_6$  electrodes:



**Fig. 15.1.** Flow electrode.

The energy consumptions for CDI and MCDI are sufficiently lower comparing with other deionization methods. This is mainly due to resulting energy consumptions. This parameter is equal to difference of energy consumptions between deionization stage (charging) and concentrating stage (discharging), since the energy is returned to the CDI and MCDI stack during the last stage (Figure 15.2 [2]).



**Figure 15.2.** MCDI scheme (a). Consumed energy costs in the deionization stage and the energy released in the regeneration stage [2] (b).

Recently a large number of papers, which dealt to investigation and optimization of CDI processes, has been published. Many of them were devoted to investigation of effect of porous structure of carbon electrodes, methods of BET and standard contact porosimetry (MSCP) were used in order to research the effect of their porous structure [5]. The MSCP technique allows us to estimate also hydrophilic and hydrophobic properties of the electrodes. It has been shown that meso-microporous carbon electrodes are more effective for deionization than microporous materials. It was shown that hydrophilization of carbon results in increase of deionization degree. For this purpose, the materials are treated with oxides of titanium, manganese or zinc. Preliminary treatment of the electrodes with KOH,  $\text{HNO}_3$  and nitrogen provides desalination

improvement. Activated carbon (AC) is the most common electrode material. However, carbon nanotubes (CNT), graphene and aerogels. In addition to symmetric electrochemical cells, for instance, AC – AC, asymmetrical cells are also used, for instance, CNT–composite CNT with polyaniline.

Many studies are devoted to removal of different ionic impurities from water, for instance, sodium, chloride, fluoride, chromate, iron, copper, arsenic, zinc, uranium, thiosulfate, organic salts and so on. Special types of carbon electrodes for selective removal of one of other ions are selected. Mathematical modeling and optimization of CDI processes are also considered [6 -8].

The approach that allows one to decrease energy consumptions of water purification was considered in [9]. The method provides usage of mosaic membrane (MM) 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 phenol-formaldehyde 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 EDL charging inside pores of the electrodes, which are 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. Thus, the idea about optimal composition of the MEA for obtaining pure water has been confirmed experimentally. The MEA has to contain MM and AC electrodes. Highly dispersive AC electrodes have to possess both cation and anion exchange capacity. The other important requirement is high surface conductivity [10]. Thus, MM application to CDI for obtaining pure water is one way to solve the problem of minimizing of the energy cost.

**Conclusions.** CDI and MSD technologies possess huge potential possibilities for water desalination. Due to the lowest energy consumptions and the largest energy recovery, these technologies are very attractive for practical usage.

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## ЄМНІСНА ДЕІОНІЗАЦІЯ ВОДИ (ОГЛЯД)

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**Резюме.** *Метод ємнісної деіонізації води (ЄДВ) полягає у прокачуванні солонатової або морської води через електрохімічну комірку, де створюється певна різниця потенціалів між вугільними електродами з великою питомою поверхнею. Цей метод є суттєво більш економічним у порівнянні з іншими опріснювальними методами, зокрема з методом зворотного осмосу. Розроблено різні модифікації ЄДВ, наприклад: мембранна ємнісна деіонізація води (МЄДВ) з катіонообмінними та аніонообмінними мембранами, ЄДВ з іонселективними вугільними електродами, ЄДВ з проточними електродами, ЄДВ з Na-інтеркалюючими електродами, ЄДВ з катіоно-аніонообмінною змішаною мембраною мозаїчної структури, яка використовується замість звичайного пористого сепаратора.*

**Ключові слова:** *ємнісна деіонізація, мозаїчна мембрана, вугільний електрод, Na-інтеркалюючий електрод, мембранна ємнісна деіонізація.*