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A. Zakharov[1], A. Tukesheva[1,2], Syed Fahad Bin Haque[3], John Ferraris[3], A. Zakhidov[3],
T. Tazhibayeva[2], T. Bazarbayeva[2], V. Pavlenko[1,2*]

[1]The Institute of Combustion Problems, Almaty, Kazakhstan;
[2] Al-Farabi Kazakh National University, Almaty, Kazakhstan;
[3]University of Texas, Dallas, USA

(e-mail: Vladimir.Pavlenko@kaznu.edu.kz)

Review of the current state of technology for capacitive deionization of aqueous salt solutions

The availability of clean water at affordable prices is one of the key technological, social, and economic challenges of the 21st century. The increased extraction of groundwater worldwide is leading to the gradual intrusion of salty water into sources and water horizons. In order to use this water for industrial and agricultural purposes, or as drinking water, it needs to be purified and desalinated. Thus, methods of desalinating water of different salinity levels, ranging from brackish to seawater, are becoming more prominent. The overall goal of current research is to make water desalination technologies more energy-efficient and cost-effective. One promising technology that meets these requirements is capacitive deionization (CDI) of water. This technology has been widely known for over 30 years, but significant progress in CDI research has only been achieved in recent years. In this review, we examine the currently developed architectures of CDI cells, advancements in carbon materials, and discuss the prospects and challenges of commercializing this technology.

Keywords: CDI, capacitive deionization, carbon materials, porous carbons, carbon electrodes, Faradaic electrodes.

Introduction

With the growth of population and the development of technological progress, humanity's water needs are increasing. At the same time, some freshwater sources are being polluted due to accidents at industrial facilities, improper waste storage, etc. Currently, almost 98 % of the available water on the earth is seawater or brackish water [1]. To use this water as technical in industries and agriculture or as drinking water, it must be preliminarily purified and desalinated. Various methods are used for desalination, among which multi-stage flash distillation (MSFD), reverse osmosis (RO), and electrodialysis (ED) are worth mentioning. The main method of industrial desalination is reverse osmosis, accounts for about 64 % of the freshwater produced, while 23 % is from multi-stage flash distillation systems, and the rest are other systems [2].

One technology that is currently being actively researched for water purification is capacitive deionization (CDI) systems. The operating principle of such system was firstly described in 1960 [3], but until the mid-2000s, the topic received poor attention by the researchers. Currently, the number of publications is growing exponentially. Compared to classical reverse osmosis, distillation, and even electrodialysis systems, capacitive purification systems have significantly lower energy consumption, lower cost, higher energy efficiency, and eco-friendliness [4–7]. The specific energy consumption for the above-mentioned systems is summarized in Table 1.

Table 1

Values of specific energy consumption for different methods of water demineralization.

Desalination method	Specific energy consumption, kW*h/m^3	Ref
Distillation	10-58	[2, 6]
Reverse osmosis	3,5-6,7	[8, 9]
Electrodialysis	0,4-8,7	[6, 10]
Capacitive deionisation	0,24-0,85	[11, 12]

Currently, CDI systems with various cell architectures and modifications of electrode materials are being actively studied. In this review, we take a look at the progress in the field of CDI systems over the past 5 years.

Various capacitive deionization cell architectures

Up to date two main fundamentally different approaches to cell assembly are proposed. These are the use of the same (symmetrical cells) or different (asymmetric cells) electrodes as the cathode and anode (Fig. 1). Classical cells with carbon electrodes are symmetrical and differ in the principle of liquid flow: through the electrodes (flow-through) or along them (flow-by). Symmetrical cells include systems upgraded with ion-exchange membranes and systems with flowing electrodes. Asymmetric cells have different electrodes, these include hybrid (carbon+faradaic electrodes) and inverse systems (carbon electrodes modified with charged functional groups).

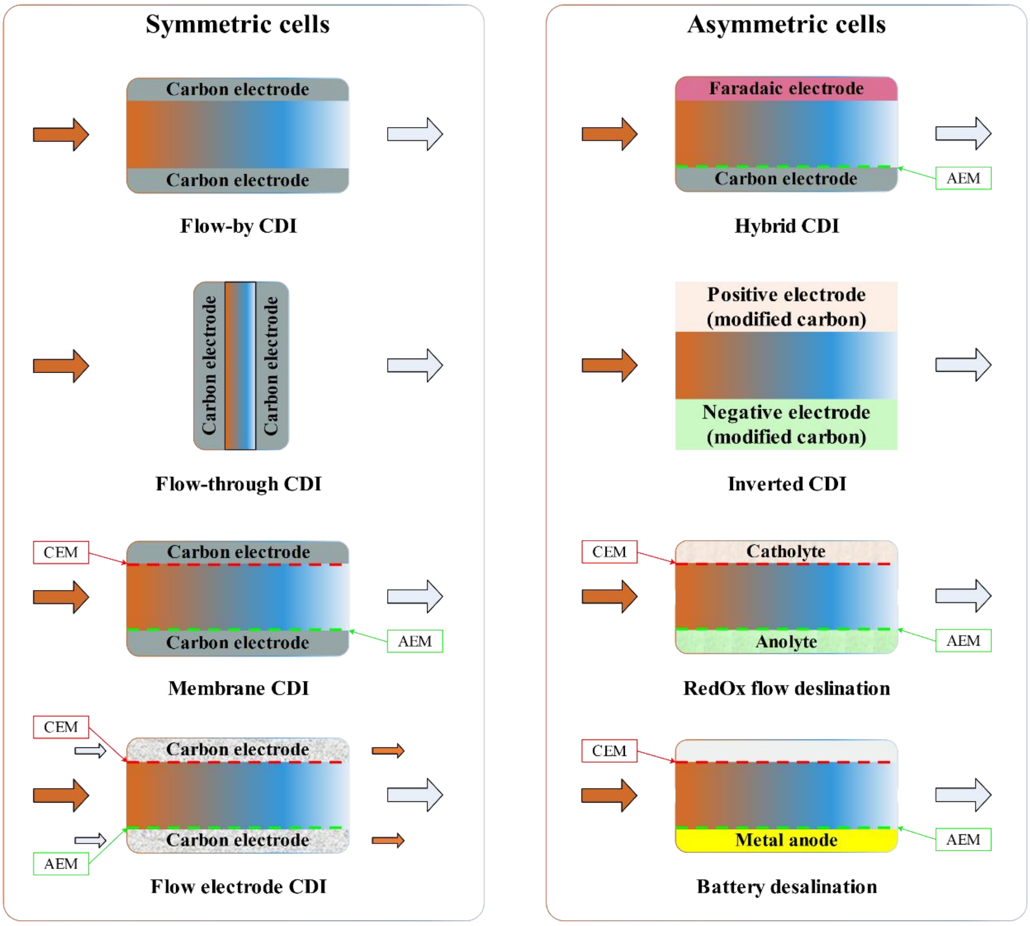

Figure 1. Basic architectures of capacitive deionization cells.

The working principle of a classic capacitive deionization cell is as follows: water is pumped between two electrodes with a potential difference of <1.4 V applied to them. Under the influence of the electric field, positively charged particles migrate to the negative electrode, and negatively charged particles migrate to the positive electrode, resulting in the formation of a double electric layer at the phase boundary. When the free surface is depleted, an inverted or zero voltage is applied to the cell. The double electric layers collapse, and the ions desorb back to the solution [9]. Two cells are required for continuous operation of a system: one cell operating in the adsorption mode and the other in the desorption mode. When the electrode surface is saturated, the cells are swapped [13].

The main problem of the classic CDI system is the secondary sorption of ions during cell regeneration step, when the applied potential is reversed. Some of the ions reach the counter electrode and were sorbed on its surface, which reduces the working capacity in the next cycle. There are two options for solving this problem: regeneration of the cell at zero potential or modernization of the system with ion-selective membranes. The first option leads to an increase in the desorption time and a decrease in the capacity of the electrodes, since not all ions can desorb under these conditions. The use of membranes is more expensive, but more efficient and makes it possible to completely eliminate cross-sorption. The membrane capacitive deionization (MCDI) cell was first described in [14] in 2006.

Capacitive deionization cells with flow electrodes (FCDI) are the next step in evolution of CDI, developed in 2013 [15]. In such cells, the electrode is not static, and the cell always operates in the adsorption mode [16]. Desorption occurs outside of the cell, through a combination with a second FCDI cell (Fig. 2), reverse osmosis system, or another purification method [9]. Typically, activated carbon suspension in an aqueous electrolyte is used as the electrode material [13]. The major problem of this system is a low charge transfer efficiency of the suspension, as the main component of the electrode is water. An obvious way to overcome this disadvantage is to increase the carbon content of the slurry, however, this leads to an increase in viscosity and a higher probability of clogging the system. The maximum achieved saturation of the slurry is 35 wt.% carbon [17]. Alternative approaches include the addition of conducting additives to the electrolyte, such as acetylene black [18, 19], NaCl [12], CNTs [20, 21].

The hybrid cell (HCDI) was first described in the mid-1960s in [22], but active research on this architecture began only in 2014 [23]. Such system consists of faradaic and capacitive electrodes. The faradaic electrode is usually used to remove sodium ions, while the capacitive electrode is used to sorb chlorine [24]. These systems are described in more detail in section devoted to non-carbon electrode materials.

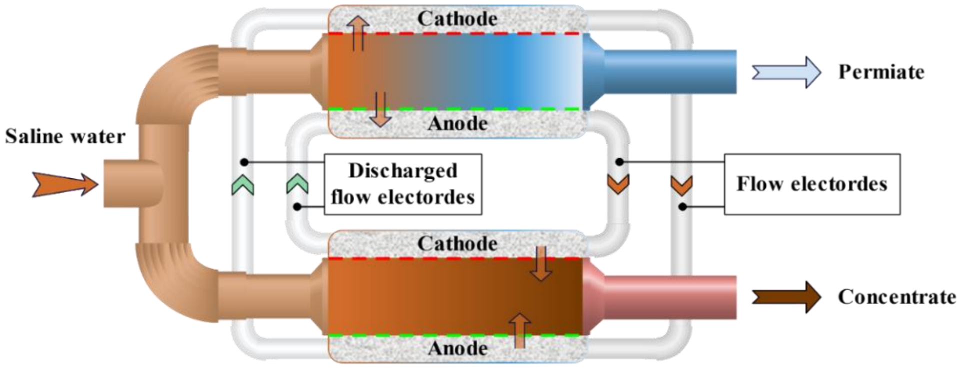

Figure 2. Schematic of the FCDI operation. The upper cell operates continuously in sorption mode, the lower cell in desorption mode.

A common problem of previously described systems is anodic oxidation, the process of formation of oxygen-containing functional compounds on the anode surface, which leads to the displacement of co-ions, and to decrease in the electrode capacity and efficiency [25]. This process is described in detail in the corresponding section below. Possible solution to this problem is to modify the positive electrode with negatively charged functional groups and the negative electrode with positive ones (ICDI). The classic methods for such modification are acid treatment or sulfonation of the positive electrode and amination of the negative. Modified electrodes are charged, so the cell is always polarized and voltage is applied only at the desorption step. Such architecture significantly reduces the total power consumption of the system [26].

Main features of CDI cells of different architectures are summarized in Table 2.

Table 2

Main features of CDI cells of different architectures.

Symmetrical architecture	Assymmetrical architecture
Flow by CDI (FB-CDI) Diffusion is the time determining process for sorption Optimization of cell dimensions is needed to maintain the required flow rate with minimum resistance.	Inverted CDI (ICDI) The cathode and anode are initially charged, so there is no need to apply the potential constantly (only during regeneration), which reduces energy costs
Flow through CDI (FTE-CDI) Less desalting time compared to FB-CDI	Flow electrode CDI (FCDI) No regeneration stage, the process is continuous
Membrane CDI (MCDI) The usage of ion-exchange membranes reduces the capture of ions during regeneration of the electrodes	Hybrid CDI (HCDI) Faradaic material with high specific capacitance Ions storage by intercalation

Carbon materials for CDI

In this review, we will focus on materials for FB-CDI, FTE-CDI, MCDI since materials used for other architectures have specific requirements in each case. For the manufacture of electrodes for cells of the above types, carbon materials are mainly used, which are characterized by a large specific surface area (high capacitance), good chemical and electrochemical stability, bioinertness, low cost, and good electrical conductivity. In many ways, these criteria are similar to the requirements for materials used in supercapacitors. Accordingly, similar mesoporous carbons, carbon fibers and fabrics, carbon nanotubes, aerogels, etc. are used in the case of CDI [27–29]. Carbon materials can be used both in pure form and modified. Modifications include doping with heteroatoms B, N, Si, P, S (individually or in combination); modifications with metal oxides — TiO_2 [30–32], MnO_2 [33, 34], ZnO [35, 36]; activation with alkalis. Various methods for modifying carbon materials are considered in details in a recent review [37].

Activated carbons are the most economically accessible materials, along with fibers and fabrics that are based on them. The surface area of such materials varies from hundreds to thousands of m^2/g, the ratio of macro-micro- and mesopores can be set at the synthesis stage. Different types of pores characterize different processes in the electrode: micropores are important for maximum sorption, mesopores for kinetics, and macropores for electrode permeability and maximization of the flow rate of purified water through the cell [27, 38–40].

Comparative characteristics of electrodes made of various carbon materials are summarized in Table 3. It should be noted that hereinafter we consider both modified and unmodified materials tested in cells for conventional capacitive deionization in the potential range of 1.0–1.4 V.

Table 3

Different carbon electrodes and its performances in CDI cells.

Electrode material type	Electrode material	Specific surface area, m^2/g	Specific capacitance, F/g	Voltage, V	NaCl solution concentration, mg/L	SAC, mg/g	Ref.
Porous carbons	CommercialAC	940	51.8	1.2	100	5.08	[41]
	OMC	844	133	1.2	–	–	[42]
	NKZCs	2566	155,83	1.2	1000	31.30	[43]
	N-HMCS/HGH	337.7	226.5	1.4	500	17.8	[44]
Carbon cloth	ACC-507-15	1339	125	1.2	–	16	[45]
	ACC	1200	–	1.2	100	5.8	[36]
	ACC/ZnO	1300	95	1.2	100	8.5	
	ACC/ZnO	1043	99	1.2	–	8.1	[46]
	ACA	2413	111.89	1.4	500	26.1	[47]
Carbon aerogel	CA	2057	156	1.2	100	29.7	[48]
Carbon nantubes and nanofibers	MO_x/CNTf	~250	50–66	1.2	250	6.5	[49]
	ACF-900	712	228	1.6	–	4.64	[50]
	ACF-900-90	1300	77	1.2	–	4.84	[51]
	CNF-600	481	1.6	1.2	2000	2	[52]
	CNF-800	579	41.8	1.2	2000	6.3	
	CNF-1000	617	52.1	1.2	2000	13.3	
Graphene-based material	RGO/ACF-10	2600	256	1.2	400	7.2	[53]
	Graphene sponge	356	205.20	1.2	500	14.9	[54]

NKZCs — novel nitrogen-rich mesoporous carbons with the zeolitic imidazolate framework-8; *N-HMCS/HGH* — N-doped hollow mesoporous carbon sphere and holey graphene hydrogel with in-plane pores; *OMC* — ordered mesoporous carbon; *ACC-507-15* — commercial activated carbon cloth textiles Kynol-507-15; *ACC* — activated carbon cloth; *ACC/ZnO* — activated carbon cloth material modified with zinc oxide nanorods; *ACA* –activated carbon aerogel; *CA* — carbon aerogel; *MO_x/CNTf* — a porous metal oxide network interpenetrated into porous fibers of carbon nanotubes; *ACF-900* — activated carbon fiber activated at 900 ˚C; *ACF-900-90* — activated carbon fiber activation processes with N_2/CO_2 at 900 °C for 90 min; *CNF-600* — carbon nanofiber carbonized at 600 °C; *CNF-800* — carbon nanofiber carbonized at 800 °C; *CNF-1000* — carbon nanofiber carbonized at 1000 °C; *RGO/ACF-10* — reduced graphene oxide (RGO) and activated carbon nanofiber composites with varying content of RGO at 10 wt.%.

Mesoporous carbons

Mesoporous carbons (MCs) are widely used as a material for CDI electrodes due to their high specific surface area, good pore size distribution, long-term stability, and low cost [55]. MCs were first applied in CDI in 2008 [42]. The authors showed that, under the same electrochemical conditions, the specific capacitance value of the MC electrode was 1.2 times higher than that of the activated carbon electrode (133 F/g and 107 F/g, respectively). In cell tests at a potential of 1.2 V and a salt solution concentration of 0.5 mg/L, the amount of adsorbed ions on the MC and activated carbon electrodes was 677.9 μg/g and 251.3 μg/g, respectively. The authors of the study attribute the better performance of MCs to the presence of pores with an optimal size (~3 nm) for ion sorption. Modern methods for producing various mesoporous carbons are summarized in recent reviews [56–58].

The main drawbacks of such materials are the need of hydrophobic binders used in the electrode formation process (which reduces the efficiency of charged particle sorption) and low conductivity. To solve the first problem, alternative binders such as PVA [59], PU [60] poly(arylene)sylphone [61], etc. are actively being developed. To solve the second problem, various modifications of the material are applied: heteroatom doping [43, 44], creation of composites with carbon nanotubes [49], modifications with semiconducting oxides [46] or the introduction of conductive additives [62].

A mesoporous carbon material with one of the best performance to date was obtained in 2020 [63], with SAC values of 23.9 mg/g, 46.3 mg/g and 83.0 mg/g for saline solutions of 250 mg/mL, 500 mg/mL and 1000 mg/L, respectively. This result is of great interest not only due to the extremely high SAC value but also because the material does not require any modifications. Thus, the average SAC value for N-modified coals is about 25 mg/g, for undoped coals it is much lower [64]. For example, in a study [43], nitrogen-rich mesoporous carbons (NKZCs) were synthesized using a zeolite imidazolate framework-8. CDI cell testing showed a SAC of 31.30 mg/g for NKZCs electrodes in a 1000 mg/L NaCl solution at 1.2V, which is higher than the carbons made from the ZIF-8/KOH composite. (SAC-20.29 mg/g) and undoped ZIF-8 (SAC-17.18 mg/g). The specific surface area of NKZCs was 2566 m^2/g, the pore volume was 1.65 cm^3/g.

A good cycling stability for mesoporous carbon-based cells is considered to be 100 cycles or more [65]. One of the records of cycling stability is a hierarchical porous carbon synthesized in [66], which has a low SAC of 13.3 mg/g and can cycle for 600 cycles without losing efficiency.

Despite the extremely wide prevalence of mesoporous carbon materials as electrodes for CDI, we have not found any recent reviews dedicated to them, except the work [67]. These materials are partially reviewed in 2017 in work [68] and in the review dedicated to metal-organic framework derived carbon for CDI [69]. We summarized some salt capacity electrosorption of various types of hierarchical carbon materials in Table 4.

Table 4

Comparison of salt capacity electrosorption of various types of hierarchical carbon materials from the literature.

CDI electrode material	Cell voltage, V	NaCl solution concentration, mg/L	SAC, mg/g	Ref.
Activated mesoporous carbon sheets	1.4	1000	3.5	[70]
Hierarchical ordered mesoporous silicon carbide-derived carbon	1.2	290	12.8	[71]
Graphene sponge	1.2	500	14.9	[54]
Hierarchically porous carbon derived from PolyHIPE	1.2	300	17.5	[72]
3D foam-like carbon nanoarchitectures	1.4	300	13.5	[73]
Carbon nanofibers reinforced 3D porous carbon polyhedra network	1.2	500	16.98	[74]
Micro/mesoporoussheets	1.2	300	15.34	[75]
3D porousgraphene	1.4	300	8.97	[76]
Hierarchicalporouscarbon	1.2	580	7.75	[77]
3D Channel-structuredgraphene	1.5	295	9.6	[78]
HierarchicalporouscarbonsHPCs	1.2	292	12.63	[79]
	1.2	292	14.0	

Carbon cloth

The second most accessible and promising material for commercial CDI cells is carbon cloth. The use of this material for electrode fabrication eliminates the need of hydrophobic polymer binders, as well as leads to simplification of the electrode manufacturing process, reducing it to cutting the material. In addition, the use of carbon fabric makes it possible to abandon the use of current collectors by connecting the contact directly to the electrode [39, 80].

Increasing the specific surface area of carbon cloth and the efficiency of salt sorption can be achieved by modifying the surface with semiconductor nanoparticles. In addition, the deposition of a semiconductor enhances the uniformity of the electric field distribution at the electrode-electrolyte interface and reduces resistance, leading to lower losses during device operation [35, 36, 46]. In [46] the authors achieved a 40 % increase in SAC (from 5.7 mg/g to 8.1 mg/g) compared to unmodified carbon cloth electrodes by surface modification with ZnO nanorods. Typical characteristic values of modified carbon cloths compared to conventional ones are presented in Table 5 [81].

Table 5

Various activated carbon cloth (ACC) electrodes and their CDI treatment performance [81].

Carbon electrode	Specific surface area, m^2/g	Cell voltage, V	NaCl solution concentration, mg/L	SAC, mg/g
ACC	984	1.6	1000	5.4
	1043	1.2	100	–
	1980	1.0	5844	1.8
	1200	1.2	100	5.8
	1980	1.2	5844	–
ACC/ZnO	1300	1.2	100	8.5
	637	1.6	1000	8.1
ACC/titania	1180	1.2	5844	8.1
	1890	1.0	5844	4.3
	546	1.2	500	–

Carbon aerogel

Carbon aerogel is one of three most commonly used materials for capacitive deionization (CDI). Aerogels were first used in CDI cells in 1995 [82]. Additional activation of carbon aerogel can improve its characteristics. For example, in the study by [47], this material was synthesized by the sol-gel method from glucose and then activated with KOH. The resulting carbon aerogels showed better characteristics (Table 6) compared to conventional carbon aerogels: the specific surface area and total pore volume increased from 567 m^2/g and 0.300 cm^3/g (activated carbon) to 2413 m^2/g and 1.389 cm^3/g (carbon aerogel), and the specific capacitance increased from 19.70 F/g to 111.89 F/g. The specific adsorption capacity values were determined during desalination of a NaCl solution with a concentration of 100 mg/L and 500 mg/L at a liquid flow rate of 30 ml/min, with a maximum SAC value of 26.1 mg/g.

Table 6

Comparison of NaCl adsorption capability of ACA electrode and other electrode materials [47].

Electrode materials	Adsorption conditions			SAC, mg/g
	Voltage, V	NaCl solution concentration, mg/L	Flow speed, ml/min	
Carbon aerogel	1.2	500	50	15.7
Porous carbons	1.2	500	30	17.2
Activated carbon	1.5	1000	50	14.6
Porous carbon spheres	1.2	500	20	15.8
Porous carbon spheres	1.6	500	50	5.8
Graphene	1.4	500	35	13.7
Graphene	1.8	100	50	4.8
Carbon sponge	1.2	500	80	16.1
Carbon nanofiber	1.2	1000	50	12.8
MoS_2–graphene	1.2	500	50	19.4
Activated carbon aerogel	*1.4*	*500*	*35*	*26.1*

Carbon aerogels possess the capacity to adsorb heavy metals as well. The authors of [48] conducted studies on the adsorption of Cu^{2+} on a carbon aerogel synthesized by the sol-gel method from resorcinol and formaldehyde. A Cu_2SO_4 solution with a concentration of 100 mg/L was used as a model, and the specific adsorption capacity (SAC) was evaluated at different potentials on the cell (0.4-1.5 V). The best result of 29.7 mg/g was obtained at a potential of 1.2 V.

However, despite the fact that aerogels have all the characteristics for CDI processes, their use is limited due to the high cost of production [67, 68].

Carbon nanotubes and nanofibers

Carbon nanotubes are a type of one-dimensional material with a hollow structure, characterized by high conductivity and good mechanical and chemical stability [83]. The high conductivity of CNTs makes it possible to use them as electrode materials and current collectors simultaneously. This also makes it possible to reduce the contact resistance and increase the power density [84]. As electrodes in CDI cells, carbon nanotubes were first used in 2005 [85].

The main problem of usage of a carbon nanotubes is the need for a binder to form the electrode. However, in the case of CNTs, alternative solutions are possible: growing directly on the surface of current collectors [86] or embedding CNTs into the carbon electrode structure [95]. For example, in [49], a CDI cell, including an anode and a cathode made of g-Al_2O_3/CNT and SiO_2/CNT, respectively, showed a SAC of 6.5 mg/g and high performance compared to a number of other materials. The authors attribute the high efficiency to the morphology of the electrodes, in which CNT fibers act simultaneously as a current collector, active material, and metal oxide substrate. This architecture exhibits high capacitance with minimal internal resistance.

Close relatives to carbon nanotubes are carbon nanofibers (CNF), which can be obtained by electrospinning method [87]. The properties of this material can be easily varied: for example, the authors of [50] changed the diameter of the obtained nanofibers within the range of 285-800 nm by varying the activation temperature from 750 to 900 °C. The obtained material had a specific surface area within the range of 335-712 m^2/g and showed a maximum SAC of 4.64 mg/g at a cell voltage of 1.6 V.

The authors of [52] showed a higher value of SAC. In this work, a carbon nanofiber was fabricated by electrospinning followed by one-stage carbonization using phenol resin as a precursor. While testing such electrodes in a CDI cell, SAC value of 50.1 mg/g at a voltage of 1.2 V was achieved, the concentration of the salt solution was 2000 mg/L. Similar values were obtained by the authors of [88]: in their work, the electrodes demonstrated a specific surface area of 3066 m^2/g, a pore volume of 2.23 cm^3/g, and a SAC of 47.22 and 63.83 mg/g in a saline solution with a concentration of 500 mg/l at potentials of 1.2 and 1.6 V, respectively.

It should be noted that despite the good characteristics of electrodes based on carbon nanotubes, their use is associated with the highest risk of developing oncological diseases (compared to other carbon materials) if particles of the material get into the treated drinking water [89].

Graphene-based electrodes

Graphene is a 2D material consisting of a monolayer of sp2-hybridized carbon atoms. Graphene has a number of unique properties, such as high mechanical strength, large specific surface area (2630 m^2/g), high charge carrier mobility, and others [90]. Despite the enormous potential of graphene as a material for electrodes in CDI cells, it is relatively rarely used. This is due to the fact that graphene monolayers can spontaneously agglomerate, which reduces the specific surface area, affects the electrode conductivity and ion transfer rate [91, 92].

One way to solve this problem is to introduce other carbon materials into the graphene matrix. For example, in [53], co-electrospinning of reduced graphene oxide and activated carbon nanofiber was used, followed by activation at 800 °C. The authors noted that the reduced graphene oxide and activated carbon nanofiber electrode exhibited SAC of 7.2 mg/g in 400 mg/L saline. The parameters of the specific surface area and pore size of the electrode made of reduced graphene oxide and activated carbon nanofiber were 621 m^2/g and 0.35 cm^3/g, respectively. Other solutions of the problem can be the doping of graphene with pyrgenic SiO_2 nanoparticles [93], the introduction of conductive polymers [94], or the bonding of graphene sheets using large functional groups [95]. A side effect of using the above methods is a drop in the stability of the composite material. It is also worth highlighting the use of crumpled graphene sheets [96, 97]. The authors of [98] showed that this solution makes it possible to obtain a material with a high specific surface area of 1568 m^2/g and a good SAC of 1.72 mg/g.

Recent advances in the field of graphene-based materials for CDI application are summarized in a number of recent reviews [99–102].

Non-carbon electrode materials

The main alternative to carbon materials in CDI are faradaic materials. These include primarily materials for electrodes in Na-ion and Cl-ion batteries, less commonly materials for Li-ion batteries and conducting polymer materials.

The most utilized materials for CDI are those used in Na-ion batteries. Among them, it is worth highlighting 1D channel structures based on α-, β-, and γ-MnO_2, layered 2D structures based on δ-MnO_2, transition metal dichalcogenides, carbides, nitrides, MXenes, and 3D structures based on λ-MnO_2. Notably, sodium manganese oxide (Na_xMnO_2) deserves separate attention due to its ability to form tunnel, layered, or mixed structures, which is dependent on the quantity of sodium [24].

In 2014, the first cell with a $Na_4Mn_9O_{18}$ anode and a porous carbon cathode separated by anion-exchange membrane was introduced [23]. When cathode was charged by a negative voltage, sodium ions were embedded in the material and released into the solution upon voltage inversion. The material had an SAC of 31.2 mg/g, which was much higher than that of a traditional activated carbon electrode at that time. This work initiated the investigation of a new class of CDI architectures — hybrid CDI.

One-dimensional materials based on manganese oxide allow to obtain a wide range of channel diameters, which can increase the selectivity of sorption for larger cations such as Ca^{2+} or Mg^{2+}. In [103], the authors obtained a material characterized by channels of various sizes, which allowed for the simultaneous accumulation of cations of different radii, such as Na^+, K^+, and Mg^{2+} (Fig. 3).

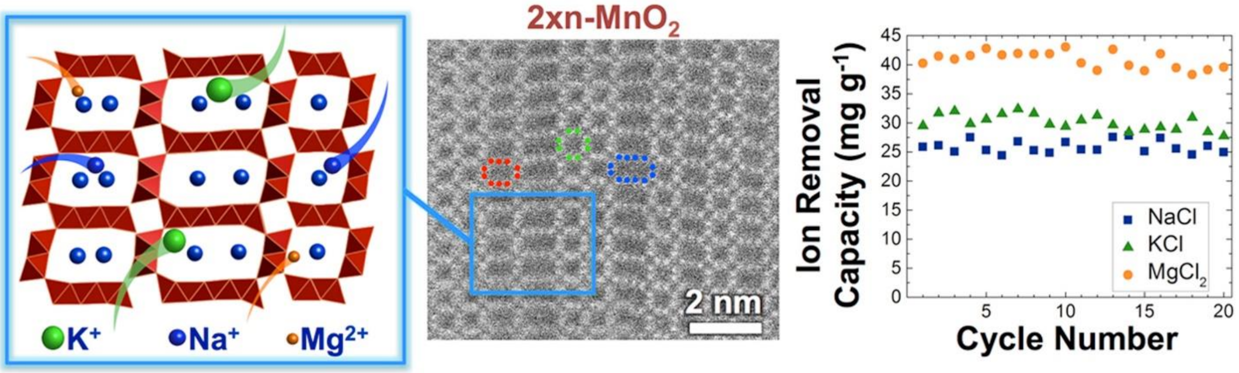

Figure 3. Scheme of available sizes for accumulating ions of various radii in a faradaic material based on MnO_2 structure [103].

Layered two-dimensional materials, such as MoS_2 [104], TiS_2 [105, 106], V_2O_5 [107], MXenes [108], etc, store ions between their layers. Some of these materials exhibit pseudocapacitive behavior and can store both cations and anions, while others show battery-like properties and can store only cations. All these materials have good specific capacitance and SAC, however, they also have a number of drawbacks. Restacking of interlayers and rapid degradation due to volume changes during intercalation-deintercalation processes are common issues [109].

Three-dimensional faradaic materials for CDI are mainly represented by NASICON structural type. Such electrodes are characterized by fantastic SAC values up to 130 mg/g [110, 111], which are unattainable for carbon materials. The main problems of NASICONs are the high selectivity (intercalation of ions other than sodium is practically impossible) and the significant volume expansion during the operation.

Faradaic materials for CDI are described in detail in a number of recent reviews [24, 64, 112], so we will not consider them. Briefly, the advantages and disadvantages of the considered types of materials for electrodes in CDI cells are summarized in Table 7.

Table 7

Advantages and disadvantages of various adsorption materials for CDI process.

Material	Advantages	Disadvantages
Mesoporous carbons	Good SAC, lowest cost, control of pore size distribution	Small pore size, high degree of pore bending
Carbon fiber and carbon cloth	Low cost, ease of processing, wide availability of commercial samples	Medium SAC, difficult technology to manufacture in the lab
Carbon aerogels	High specific surface area, control of pore size distribution	High costs
Carbon nanotubes and nanofibers	High surface area, great electrical conductivity, high cycling stability	High tendency to aggregate (drop in specific surface area), need for hydrophobic binder, low SAC
Graphene	High surface area, great electrical conductivity	Extreme tendency to aggregation (drop in specific surface area, SAC, etc)
Metal-carbon materials	High specific capacitance, wettability and good electrochemical performance	Complicated production process and high cost
Faradaic materials	Very high specific capacitance and SAC	Complicated production process and high cost Insufficient cyclic stability, high selectivity, significant volumetric expansion of the material

To sum up, there are following trends in the development of carbon materials for CDI: currently, the best results are achieved with classical mesoporous carbons, although the average specific adsorption capacity (SAC) of 25 mg/g for this type of material is still relatively low. Recently, materials with various modifications have been actively studied, including N and B doping, development of composite materials that include both classical carbon and nanoscale materials, and the active exploration of possibilities for transitioning from classical binders (such as PVDF) to more hydrophobic ones. However, there are also harmful trends: when multiple modifications are introduced in pursuit of improving one characteristic, authors often lose ground in others. Therefore, we would like to emphasize the need for a rational approach in the design and development of new materials [113].

The use of faradaic materials as electrodes for CDI seems to be more promising in terms of seawater desalination. Such materials currently allow the desalination of much more concentrated solutions in comparison with classical carbon materials. Nevertheless, this direction has its own peculiarities, among which it is necessary to highlight the extremely high selectivity for the removal of Na^+ and Cl^- ions, which does not allow most materials to be used for water purification from heavy metals and associated ions. The second feature is the presence of a small amount of faradaic materials suitable for capturing Cl^- anions. In fact, currently there are only 3 materials for Cl^- storage in CDI systems: these are MXenes [108], BiOCl [114] and Ag [115]. Adapting other materials used in batteries for Cl^- storage seems to be a promising task. The third feature is that due to the specificity of materials and processes involved, symmetric CDI cells cannot always be created. This leads to the fact that different amounts of electrons may be required to remove ions of opposite charge [114], which means that without additional optimization and synchronization of the processes occurring at the electrodes, such CDI cells will have a reduced desalination efficiency. However, most current research ignores the issue of cell balancing, both in the case of Faraday and carbon electrode materials, focusing solely on the efficiency of the finished system. We highly recommend performing individual ion capture studies for each electrode and optimizing finished cells.

A separate problem is the degradation of electrode materials during operation. And if for faradaic materials this problem is associated with a change in volume during operation and is universal for CDI and batteries, then for carbon materials this problem is unique and does not manifest itself in other applications. We will discuss this issue in details in the next section.

Degradation of electrodes

The most common process of electrode degradation is the process of anodic oxidation, when oxygen-containing functional groups are formed on the surface of the electrode. The reactions describing this process are presented below [64]:

$C + H_2O \rightarrow C{=}O + 2\ H^+ + 2e^-$

$C + H_2O \rightarrow C\text{-}OH + H^+ + e^-$

$C + 2\ H_2O \rightarrow CO_2 + 4\ H^+ + 4e^-$, $E^0 = 0.21$ V/SHE

First, the formation of functional groups disrupts the uniform distribution of potential both on the electrode surfaces and between them, leading to faster cell wear. Second, the formation of new groups reduces the available surface area and pore volume. Finally, this undesirable surface modification leads to an “inversion effect”, which is characterized by the displacement of anions from the surface of the charged cell, resulting in a decrease in efficiency [25, 116]. The authors of [117] observed this phenomenon during cycling of a symmetric cell in the +1.2/0 V mode, which led to a decrease in the SAC index from 7.3 to 0.5 mg/g over 70 cycles. Transitioning from a symmetric to an asymmetric cell and optimizing the operating mode (+0.8/-0.4 V) increased cyclability to over 120 cycles without loss of effectiveness while maintaining SAC of 6.3 mg/g. In [118] it is shown that activated carbon tissue undergoes oxidation in Na_2SO_4 or KH_2PO_4/KOH buffer solutions at potentials ranging from -1.5 to 5.0 V. The Table 7 summarizes XPS data, BET surface area determinations, and pH at the point of zero charge for samples subjected to various conditions. It can be seen that the available surface area decreases with increasing applied potential and simultaneous changes in the C and O contents in favor of the formation of oxygen-containing groups on the surface (Table 8). The shift in pH at point of zero charge (pH_{PZC}) from 7.40 to 3.21 also indicates an increase in surface acidity. Based on the research results, the authors propose an optimal range of potentials from -1.5 V to +0.8 V, which is significantly lower than the classical potential values on the cell in the sorption mode (+1.2-1.6 V).

Table 8

Surface textural properties of pristine and polarization treated ACC samples [118].

Sample	S_{BET}, m^2/g	V_{tot}, cm^3/g	C	H	O	pH_{PZC}
ACC	1596	0.697	85.9	1.13	13.0	7.40
ACC + 0.5	1549	0.671	85.1	1.12	13.8	6.83
ACC + 0.8	1541	0.655	81.4	1.15	17.4	6.34
ACC + 1.5	1488	0.652	76.8	1.45	21.8	3.95
ACC + 5.0	1300	0.559	68.3	0.98	30.8	3.21
ACC − 1.5	1518	0.662	84.4	1.14	13.3	7.32

The second undesirable process is cathodic reduction, characterized by the following reactions:

$O_2 + 2\ H^+ + 2e^- \rightarrow H_2O_2$, $E^0 = 0.69$ V/SHE

$H_2O_2 + 2\ H^+ + 2e^- \rightarrow 2\ H_2O$, $E^0 = 1.78$ V/SHE

$O_2 + 4\ H^+ + 4e^- \rightarrow 2\ H_2O$, $E^0 = 1.23$ V/SHE

It can be seen that the main process here is a two-electron transfer with the formation of hydrogen peroxide, which is a strong oxidizing agent. The formation of H_2O_2 in the system further exacerbates the anodic oxidation process. There are several options for solving this problem: modification of the surface of a carbon material [119, 120], the use of membrane technologies [121], which prevent the access of oxygen to the electrode, or the transition to inversion CDI [26]. However, these solutions have their drawbacks: for example, the use of ion-selective membranes and modification of electrodes significantly increase the cost of the device, and iCDI devices cannot compete with classical systems yet.

Regarding non-carbon materials, they are not subjected to oxidation processes during device operation, however, they have their own issues related to the volume change during ion intercalation/deintercalation [24].

Commercial prototypes

Large-scale commercial applications of CDI cells are rarely discussed in major reviews, indicating that the technology is still in its early stages. Nevertheless, the number of patents with the C02F1/4691 code (treatment of water, waste water, or sewage by electrochemical methods; by electrochemical separation, e.g. by electro-osmosis, electrodialysis, electrophoresis; capacitive deionization) has been growing exponentially in the past 25 years (Fig. 4). The leader in the field is China with approximately 40 % of published patents, followed by South Korea and the US, each with about 19 %. Approximately 9 % of the patents belong to European countries and WIPO, while the remaining countries account for less than 5 % of the patents (Fig. 4). These data collectively indicate the potential of the technology and the interest of the global community in its development.

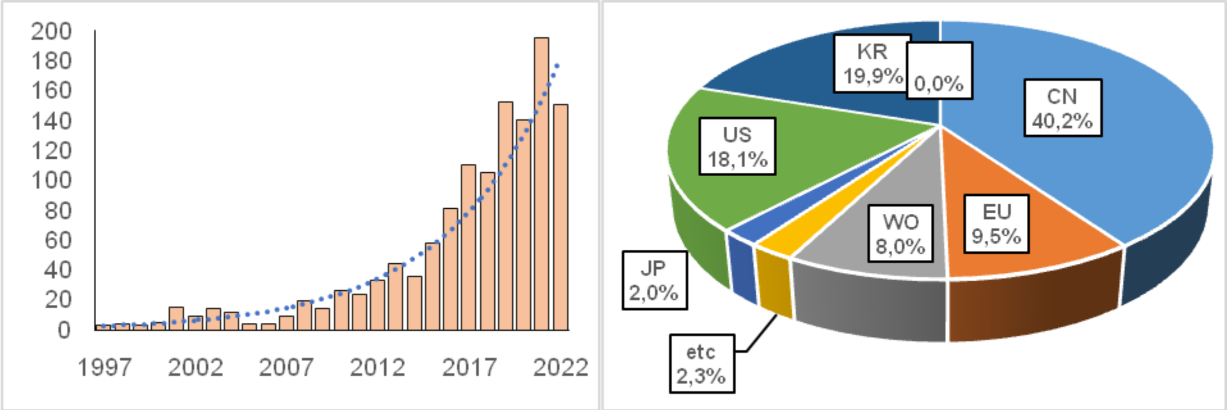

Figure 4. The number of published patents with C02F1/4691 classifier since 1997 till 2022 (left) and the ratio of country codes in these patents (right). CN — China, EU — European countries, WO — WIPO, JP — Japan, US — United States, KR — South Korea, etc. — other countries.

Interestingly, that among the data we analyzed, patents with flow-by cell geometry are rare, in contrast to scientific articles, where such a geometry is used almost universally. As we pointed out at the beginning of the review, the flow-through geometry does not require optimization of the dimensions of the fluid flow channel and separator, which, apparently, simplifies the scaling of the system.

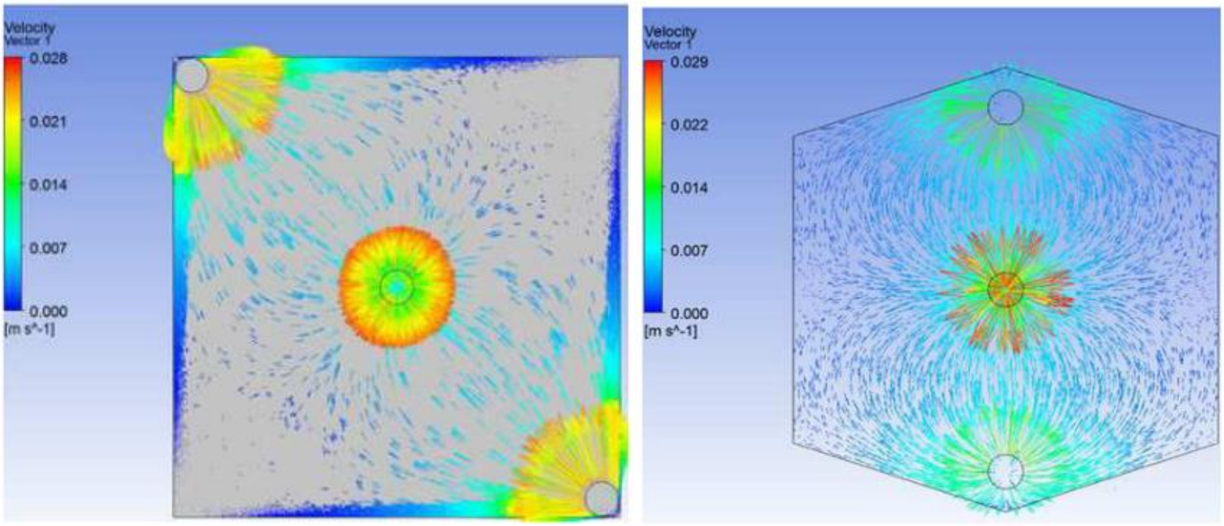

Figure 5. Calculated fluid flow vectors in the square (left) and hexagonal (right) CDI cells [122].

Most of the patents concerning the assembly of the CDI system describe conventional cells [123–125] or MCDI cells [126–128], in recent years FCDI cells [129–131] have also been represented. We have not found any patents for systems with asymmetric electrode geometry. In addition to systems that include only a CDI cell, various combinations of purification systems are also described: ED-CDI [132, 133], FO-CDI [134], RO-CDI [128, 135], PVD-CDI [136], etc.

A lot of patents do not provide any information about any tests of described systems, which makes it difficult to analyze and evaluate the data provided. Nevertheless, we have tried to select a number of works that are interesting from our point of view, concerning configurations and assembly of prototypes. In particular, patent [123] describes the procedure for assembling a conventional CDI cell with an optimized desalination efficiency of 93 %. Liquid inlet is carried out along the plane of the electrodes, outlet from the center, perpendicular to the plane. We did not find such a cell geometry in scientific articles, but it is not rare in patents [127, 137]. The work [122] describes the optimization of the shape of the flow chamber of the cell, it is shown that the hexagonal shape makes it possible to achieve a much more uniform liquid flow, which increases the purification efficiency (Fig. 5).

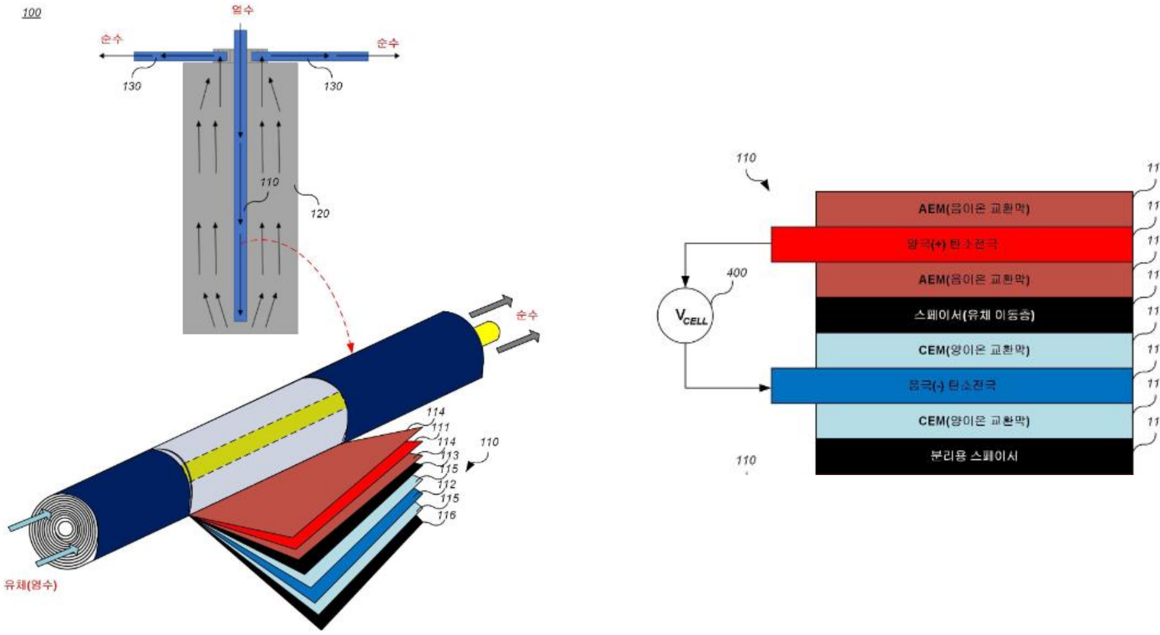

Figure 6. Schematic of a cylindrical CDI module with a winding of a six-layer MCDI [127].

Multilayer cylindrical modules [127] represent another intriguing solution. For this, a six-layer flexible MCDI with two separators (Fig. 6) is assembled, which is wound around the hollow central axis of a cylindrical container. The scheme of fluid flow through the module is shown in Figure 7. Variation of the number of layers makes it easy to control the capacity of the module, the winding process is widely used technologically and does not require the development of additional systems. The procedure for fabricating flexible electrodes for MCDI is described in a patent [129].

Another solution we did not find in the scientific articles is to increase the working area of the electrodes by corrugation [137]. However, this solution seems inefficient, since it entails an increase in the thickness of one module, which leads to an increase in the cost of a full-size installation. FCDI patents mainly describe the general principles for creating such systems, the most interesting prototype is described in [131] with a desalination efficiency of 75 %.

A semi-industrial CDI system available on the international market is the CapDI system manufactured by Voltea [125, 138–140]. System modules are an assembly of several square MCDI cells. Liquid inlet is carried out through 2 holes on opposite square edges, outlet is manufactured through the central hole. The average voltage on the cell is 1 V, the efficiency of desalination is 25-90 %, depending on the characteristics of the source water.

Summary and outlook

Currently, CDI technology is one of the most energy-efficient and cost-effective technologies for desalinating brackish and, in near future, seawater, which makes it extremely attractive for researchers around the world. Ideal materials that can be used as electrodes in CDI systems are various carbon materials similar to those used in supercapacitors. Their comprehensive research has been actively carried out for several decades, and to date there is a huge number of options for various carbon materials suitable for use in CDI systems. The use of well-studied faradaic materials has allowed for further increases in SAC and has shown potential for desalination not only of brackish water but also seawater.

The main methods for improving the characteristics of both carbon and faradaic materials are the methods of modification of bulk material or its surface. However, there are not many studies devoted to the purification of not ideal solutions based on NaCl, but real samples or at least model systems consisting of various ions. This is especially true for works dedicated to faradaic electrodes that have high selectivity for Na^+ ions. Also, many researchers in the pursuit of improving one characteristic lose in a number of others, which indicates the insufficient use of rational approaches to design and obtaining new materials for electrodes in CDI cells. In addition, it should be noted that there are only a few works devoted to optimizing cell geometries, studying processes occurring in the pre-electrode space, and mechanisms underlying ion sorption/intercalation. Such neglect of fundamental research leads to the underestimation of key indicators of

CDI systems, as researchers often conduct tests of unoptimized systems. In articles devoted to the study of hybrid cells based on faradaic and carbon materials, the absence of balancing the cathode and anode is often encountered, although the processes occurring on them are fundamentally different. We urge researchers to conduct their work more carefully and take these aspects into account. We would also like to draw the attention of researchers to the lack of unified protocols for testing CDI cells, the use of different SAC designations and different units for measuring the concentrations of starting salt solutions, which makes it difficult to evaluate and analyze published works.

Commercial use of CDI cells is currently in its early stages. However, there is a certain interest in this direction: the number of patents related to this technology is steadily increasing and in recent years it has been around 200 works per year. In recent years, works [141, 142] have been published on the techno-economic analysis of CDI technology compared to alternative water purification methods, which have shown that there are several challenges on the path to successful commercialization of the technology. The main challenge is electrode degradation caused by anodic oxidation in the case of carbon materials and volume changes during cycling in the case of faradaic materials. To a large extent, this problem can be solved by ion exchange membranes, but this leads to a complication of the system and an increase in its cost. Solving these problems at a fundamental level will make it possible to significantly increase cell cycling, reduce depreciation costs and move CDI technology to a fundamentally new level.

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References

1 Fry, L.M., Mihelcic, J.R. & Watkins, D.W. (2008). Water and nonwater-related challenges of achieving global sanitation coverage. *Environ. Sci. Technol., Vol. 42*(12), P. 4298–4304.

2 Borsani, R. & Rebagliati, S. (2005). Fundamentals and costing of MSF desalination plants and comparison with other technologies. *Desalination, Vol. 182,* 1–3, P. 29–37.

3 Murphy, G.W. & Tucker, J.H. (1966). The demineralization behavior of carbon and chemically-modified carbon electrodes. *Desalination, Vol. 1*(3), P. 247–259.

4 Greenlee, L.F. et al. (2009). Reverse osmosis desalination: Water sources, technology, and today's challenges. *Water Research, Vol. 43*(9), P. 2317–2348.

5 Strathmann, H. (2010). Electrodialysis, a mature technology with a multitude of new applications. *Desalination, Vol. 264*(3), P. 268–288.

6 AlMarzooqi, F.A. et al. (2014). Application of Capacitive Deionisation in water desalination: A review. *Desalination, Vol. 342,* P. 3–15.

7 Kang, J. et al. (2014). Comparison of salt adsorption capacity and energy consumption between constant current and constant voltage operation in capacitive deionization. *Desalination, Vol. 352,* P. 52–57.

8 Zhao, R. et al. (2013). Energy consumption in membrane capacitive deionization for different water recoveries and flow rates, and comparison with reverse osmosis. *Desalination, Vol. 330,* P. 35–41.

9 Folaranmi, G. et al. (2020). Towards electrochemical water desalination techniques: a review on capacitive deionization, membrane capacitive deionization and flow capacitive deionization. *Membranes, Vol. 10*(5), P. 96.

10 Turek, M. (2003). Cost effective electrodialytic seawater desalination. *Desalination, Vol. 153,* 1–3, P. 371–376.

11 Ma, J. et al. (2020). Free-standing Ti3C2Tx MXene film as binder-free electrode in capacitive deionization with an ultrahigh desalination capacity. *Chemical Engineering Journal, Vol. 384,* P. 123329.

12 Yang S. et al. (2016). Flow-Electrode Capacitive Deionization Using an Aqueous Electrolyte with a High Salt Concentration. *Environ. Sci. Technol, Vol. 50*(11), P. 5892–5899.

13 Volfkovich, Yu.M. (2020). Capacitive deionization of water (a review). *Russ J Electrochem, Vol. 56*(1), P. 18–51.

14 Lee, J.-B. et al. (2006). Desalination of a thermal power plant wastewater by membrane capacitive deionization. *Desalination, Vol. 196*(1), P. 125–134.

15 Jeon, S. et al. (2013). Desalination via a new membrane capacitive deionization process utilizing flow-electrodes. *Energy Environ. Sci, Vol. 6*(5), P. 1471.

16 Rommerskirchen, A. et al. (2020). Flow-electrode capacitive deionization enables continuous and energy-efficient brine concentration. *Desalination, Vol. 490,* P. 114453.

17 Park, H. et al. (2016). Surface-modified spherical activated carbon for high carbon loading and its desalting performance in flow-electrode capacitive deionization. *RSC Adv, Vol. 6*(74), P. 69720–69727.

18 Hatzell, K.B. et al. (2014). Capacitive deionization concept based on suspension electrodes without ion exchange membranes. *Electrochemistry Communications, Vol. 43,* P. 18–21.

19 Liang, P. et al. (2017). Optimized desalination performance of high voltage flow-electrode capacitive deionization by adding carbon black in flow-electrode. *Desalination, Vol. 420,* P. 63–69.

20 Li, H. et al. (2011). A comparative study on electrosorptive behavior of carbon nanotubes and graphene for capacitive deionization. *Journal of Electroanalytical Chemistry, Vol. 653*(1), P. 40–44.

21 Cho, Y. et al. (2019). Flow-electrode capacitive deionization with highly enhanced salt removal performance utilizing high-aspect ratio functionalized carbon nanotubes. *Water Research, Vol. 151,* P. 252–259.

22 Murphy, G.W. & Caudle, D.D. (1967). Mathematical theory of electrochemical demineralization in flowing systems. *Electrochimica Acta, Vol. 12*(12), P. 1655–1664.

23 Lee, J. et al. (2014). Hybrid capacitive deionization to enhance the desalination performance of capacitive techniques. *Energy Environ. Sci, Vol. 7*(11), P. 3683–3689.

24 Li, Q. et al. (2020). Faradaic Electrodes Open a New Era for Capacitive Deionization. *Adv. Sci, Vol. 7*(22), P. 2002213.

25 Che, X. et al. (2019). Inverted Capacitive Deionization with Highly Enhanced Stability Performance Utilizing Ionic Liquid-Functionalized Carbon Electrodes. *ACS Sustainable Chem. Eng. American Chemical Society, Vol. 7*(18), P. 15715–15722.

26 Gao, X. et al. (2015). Surface charge enhanced carbon electrodes for stable and efficient capacitive deionization using inverted adsorption–desorption behavior. *Energy Environ. Sci, Vol. 8*(3), P. 897–909.

27 S. Bagotsky, V., M. Skundin, A. & M. Volfkovich, Y. (2014). Electrochemical power sources: Batteries, fuel cells, and supercapacitors. *Hoboken, NJ, USA: John Wiley & Sons, Inc.*

28 Porada, S. et al. (2013). Review on the science and technology of water desalination by capacitive deionization. *Progress in Materials Science, Vol. 58*(8), P. 1388–1442.

29 Jia, B. & Zhang, W. (2016). Preparation and application of electrodes in capacitive deionization (CDI): a state-of-art review. *Nanoscale Res Lett, Vol. 11*(1), P. 64.

30 Chang, L.M., Duan, X.Y. & Liu, W. (2011). Preparation and electrosorption desalination performance of activated carbon electrode with titania. *Desalination, Vol. 270,* 1–3, P. 285–290.

31 Ryoo, M.-W. & Seo, G. (2003). Improvement in capacitive deionization function of activated carbon cloth by titania modification. *Water Research, Vol. 37*(7), P. 1527–1534.

32 Ryoo, M.-W., Kim, J.-H. & Seo, G. (2003). Role of titania incorporated on activated carbon cloth for capacitive deionization of NaCl solution. *Journal of Colloid and Interface Science, Vol. 264*(2), P. 414–419.

33 Liu, Y.-H. et al. (2016). Electrodeposited Manganese Dioxide/Activated Carbon Composite As a High-Performance Electrode Material for Capacitive Deionization. A*CS Sustainable Chem. Eng., Vol. 4*(9), P. 4762–4770.

34 Wu, T. et al. (2018). Highly Stable Hybrid Capacitive Deionization with a MnO 2 Anode and a Positively Charged Cathode. *Environ. Sci. Technol. Lett., Vol. 5*(2), P. 98–102.

35 Laxman, K. et al. (2015). Effect of a semiconductor dielectric coating on the salt adsorption capacity of a porous electrode in a capacitive deionization cell. *Electrochimica Acta, Vol. 166,* P. 329–337.

36 Myint, M.T.Z., Al-Harthi, S.H. & Dutta, J. (2014). Brackish water desalination by capacitive deionization using zinc oxide micro/nanostructures grafted on activated carbon cloth electrodes. *Desalination, Vol. 344,* P. 236–242.

37 Cheng, Y. et al. (2019). A review of modification of carbon electrode material in capacitive deionization. *RSC Adv., Vol. 9*(42), P. 24401–24419.

38 Pandolfo, A.G., & Hollenkamp, A.F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources, Vol. 157*(1), P. 11–27.

39 Kim, C. et al. (2017). Influence of pore structure and cell voltage of activated carbon cloth as a versatile electrode material for capacitive deionization. *Carbon, Vol. 122,* P. 329–335.

40 Liu, P.-I. et al. (2015). Effects of activated carbon characteristics on the electrosorption capacity of titanium dioxide/activated carbon composite electrode materials prepared by a microwave-assisted ionothermal synthesis method. *Journal of Colloid and Interface Science, Vol. 446,* P. 352–358.

41 Liu, N.-L., Sun, S.-H., & Hou, C.-H. (2019). Studying the electrosorption performance of activated carbon electrodes in batch-mode and single-pass capacitive deionization. *Separation and Purification Technology, Vol. 215,* P. 403–409.

42 Zou, L. et al. (2008). Using mesoporous carbon electrodes for brackish water desalination. *Water Research, Vol. 42,* 8–9. P. 2340–2348.

43 Zhao, Y. et al. (2019). Nitrogen-rich mesoporous carbons derived from zeolitic imidazolate framework-8 for efficient capacitive deionization. *Electrochimica Acta, Vol. 321,* P. 134665.

44 Mi, M. et al. (2019). Hierarchical composite of N-doped carbon sphere and holey graphene hydrogel for high-performance capacitive deionization. *Desalination, Vol. 464,* P. 18–24.

45 Kim, C. et al. (2017). Influence of pore structure and cell voltage of activated carbon cloth as a versatile electrode material for capacitive deionization. *Carbon, Vol. 122,* P. 329–335.

46 Myint, M.T.Z. & Dutta, J. (2012). Fabrication of zinc oxide nanorods modified activated carbon cloth electrode for desalination of brackish water using capacitive deionization approach. *Desalination, Vol. 305,* P. 24–30.

47 Wang, W. et al. (2022). Activated carbon aerogel as an electrode with high specific capacitance for capacitive deionization. *Processes, Vol. 10*(11), P. 2330.

48 Cao, Z. et al. (2019). Preparation of carbon aerogel electrode for electrosorption of copper ions in aqueous solution. *Materials, Vol. 12*(11), P. 1864.

49 Santos, C. et al. (2018). Interconnected metal oxide CNT fibre hybrid networks for current collector-free asymmetric capacitive deionization. *J. Mater. Chem. A. Vol. 6*(23), P. 10898–10908.

50 Wang, G. et al. (2012). Activated carbon nanofiber webs made by electrospinning for capacitive deionization. *Electrochimica Acta, Vol. 69,* P. 65–70.

51 Liu, N.-L. et al. (2020). Enhanced desalination of electrospun activated carbon fibers with controlled pore structures in the electrosorption process. *Environ. Sci.: Water Res. Technol., Vol. 6*(2), P. 312–320.

52 Chen, Y. et al. (2014). Electrospun carbon nanofiber networks from phenolic resin for capacitive deionization. *Chemical Engineering Journal, Vol. 252,* P. 30–37.

53 Dong, Q. et al. (2014). Electrospun composites made of reduced graphene oxide and activated carbon nanofibers for capacitive deionization. *Electrochimica Acta, Vol. 137,* P. 388–394.

54 Xu, X. et al. (2015). Facile synthesis of novel graphene sponge for high performance capacitive deionization. *Sci Rep., Vol. 5(1),* P. 8458.

55 Lu, P. -J. et al. (2011). Chemical regeneration of activated carbon used for dye adsorption. *Journal of the Taiwan Institute of Chemical Engineers, Vol. 42*(2), P. 305–311.

56 Mehdipour-Ataei, S. & Aram, E. (2023). Mesoporous Carbon-Based Materials: A Review of Synthesis, Modification, and Applications. *Catalysts, Vol. 13*(1).

57 Pavlenko, V. et al. (2022). A comprehensive review of template-assisted porous carbons: Modern preparation methods and advanced applications. *Materials Science and Engineering: R: Reports, Vol. 149,* P. 100682.

58 Weng, J. et al. (2021). A review of metal-organic framework-derived carbon electrode materials for capacitive deionization. *New Carbon Materials, Vol. 36*(1), P. 117–132.

59 Weng, J. et al. (2021). Carbon electrode with cross-linked and charged chitosan binder for enhanced capacitive deionization performance. *Desalination, Vol. 505,* P. 114979.

60 Yen, C.H. et al. (2021). Titanium Dioxide/Activated Carbon Electrode with Polyurethane Binder for the Removal of Indium Ions via Capacitive Deionization. *Processes, Vol. 9*(8), P. 1427.

61 Asquith, B.M., Meier-Haack, J. & Ladewig, B.P. (2015). Poly (arylene ether sulfone) copolymers as binders for capacitive deionization activated carbon electrodes. *Chemical Engineering Research and Design, Vol. 104,* P. 81–91.

62 Park, K.-K. et al. (2007). Development of a carbon sheet electrode for electrosorption desalination. *Desalination, Vol. 206,* 1–3, P. 86–91.

63 Zhang, P., Li, J. & Chan-Park, M.B. (2020). Hierarchical Porous Carbon for High-Performance Capacitive Desalination of Brackish Water. *ACS Sustainable Chem. Eng. American Chemical Society, Vol. 8*(25), P. 9291–9300.

64 Sun, K. et al. (2023). Electrocapacitive Deionization: Mechanisms, Electrodes, and Cell Designs. *Adv Funct Materials.* P. 2213578.

65 Geng, C. et al. (2022). Continuous cycling of carbon-based capacitive deionization systems: An evaluation of the electrode performance and stability. *Journal of Electroanalytical Chemistry, Vol. 914,* P. 116298.

66 Baroud, T.N. & Giannelis, E.P. (2018). High salt capacity and high removal rate capacitive deionization enabled by hierarchical porous carbons. *Carbon. Vol. 139,* P. 614–625.

67 Datar, S.D., Mane, R. & Jha, N. (2022). Recent progress in materials and architectures for capacitive deionization: A comprehensive review. *Water Environment Research, Vol. 94*(3).

68 Huang, Z.-H. et al. (2017). Carbon electrodes for capacitive deionization. *J. Mater. Chem. A. Vol. 5*(2), P. 470–496.

69 Wang, H. et al. (2022). Nanoarchitectonics of Metal–Organic Frameworks for Capacitive Deionization via Controlled Pyrolyzed Approaches. *Small. Vol. 18*(2), P. 2102477.

70 Tsouris, C. et al. (2011). Mesoporous carbon for capacitive deionization of saline water. *Environ. Sci. Technol., Vol. 45*(23), P. 10243–10249.

71 Porada, S. et al. (2013). Direct prediction of the desalination performance of porous carbon electrodes for capacitive deionization. *Energy Environ. Sci., Vol. 6*(12), P. 3700.

72 Xu, X. et al. (2016). Design and fabrication of mesoporous graphene via carbothermal reaction for highly efficient capacitive deionization. *Electrochimica Acta, Vol. 188,* P. 406–413.

73 El-Deen, A.G. et al. (2016). Flexible 3d nanoporous graphene for desalination and bio-decontamination of brackish water via asymmetric capacitive deionization. *ACS Appl. Mater. Interfaces. Vol. 8*(38), P. 25313–25325.

74 Liu, Y. et al. (2016). Electrospun carbon nanofibers reinforced 3D porous carbon polyhedra network derived from metal-organic frameworks for capacitive deionization. *Sci Rep., Vol. 6*(1), P. 32784.

75 Jia, B., & Zou, L. (2012). Graphene nanosheets reduced by a multi-step process as high-performance electrode material for capacitive deionisation. *Carbon, Vol. 50*(6), P. 2315–2321.

76 Hu, W. et al. (2017). Hierarchically porous carbon derived from PolyHIPE for supercapacitor and deionization applications. Langmuir. Vol. *33*(46), P. 13364–13375.

77 Duan, H. et al. (2017). Rapid construction of 3D foam-like carbon nanoarchitectures via a simple photochemical strategy for capacitive deionization. *RSC Adv. Vol. 7*(62), P. 39372–39382.

78 Chang, L. & Hang, Hu.Y. (2019). 3D Channel-structured graphene as efficient electrodes for capacitive deionization. *Journal of Colloid and Interface Science, Vol. 538,* P. 420–425.

79 Baroud, T. & Giannelis, E. (2019). Role of Mesopore Structure of Hierarchical Porous Carbons on the Electrosorption Performance of Capacitive Deionization Electrodes. *ACS Sustainable Chemistry & Engineering, Vol. 7.*

80 Zhao, X. et al. (2020). Electrode materials for capacitive deionization: A review. *Journal of Electroanalytical Chemistry, Vol. 873,* P. 114416.

81 Maddah, H.A. & Shihon, M.A. (2018). Activated carbon cloth for desalination of brackish water using capacitive deionization. Desalination and Water Treatment. Ed. Eyvaz M., Yüksel E. InTech.

82 Farmer, J.C. et al. (1995). The use of capacitive deionization with carbon aerogel electrodes to remove inorganic contaminants from water: UCRL-JC—119844, CONF-950718—1, 80970. P. UCRL-JC—119844, CONF-950718—1, 80970.

83 Pan, H., Li, J. & Feng, Y.P. (2010). Carbon nanotubes for supercapacitor. *Nanoscale Res Lett., Vol. 5*(3), P. 654–668.

84 Frackowiak, E. & Béguin, F. (2001). Carbon materials for the electrochemical storage of energy in capacitors. *Carbon, Vol. 39*(6), P. 937–950.

85 Dai, K. et al. (2005). NaCl adsorption in multi-walled carbon nanotubes. *Materials Letters. Vol. 59*(16), P. 1989–1992.

86 Wang, H. & Na, C. (2014). Binder-Free Carbon Nanotube Electrode for Electrochemical Removal of Chromium. *ACS Appl. Mater. Interfaces. American Chemical Society, Vol. 6*(22), P. 20309–20316.

87 Kim, B.-H. et al. (2011). Solvent-induced porosity control of carbon nanofiber webs for supercapacitor. *Journal of Power Sources.*

88 Zhang, H. et al. (2023). Highly mesoporous carbon nanofiber electrodes with ultrahigh specific surface area for efficient capacitive deionization. *Carbon. Vol. 201,* P. 920–929.

89 Donaldson, K. et al. (2006). Carbon Nanotubes: A Review of Their Properties in Relation to Pulmonary Toxicology and Workplace Safety. *Toxicological Sciences, Vol. 92(1), P. 5–22.*

90 Huang, Y., Liang, J. & Chen, Y. (2012). An Overview of the Applications of Graphene-Based Materials in Supercapacitors. *Small, Vol. 8*(12), P. 1805–1834.

91 Dreyer, D.R., Todd, A.D. & Bielawski, C.W. (2014). Harnessing the chemistry of graphene oxide. *Chem. Soc. Rev, Vol. 43*(15), P. 5288.

92 Li, Z. et al. (2015). 3D porous graphene with ultrahigh surface area for microscale capacitive deionization. *Nano Energy, Vol. 11,* P. 711–718.

93 Kim, D.W., Jung, S.M. & Jung, H.Y. (2020). Long term thermostable supercapacitor using in-situ SnO2 doped porous graphene aerogel. *Journal of Power Sources. Vol. 448,* P. 227422.

94 Zhai, Z. et al. (2022). A review of carbon materials for supercapacitors. *Materials & Design, Vol. 221,* P. 111017.

95 Greenwood, J. et al. (2015). Covalent Modification of Graphene and Graphite Using Diazonium Chemistry: Tunable Grafting and Nanomanipulation. *ACS Nano, Vol. 9*(5), P. 5520–5535.

96 Yan, J. et al. (2012). High-performance supercapacitor electrodes based on highly corrugated graphene sheets. *Carbon, Vol. 50*(6), P. 2179–2188.

97 Wen, Z. et al. (2012). Crumpled Nitrogen-Doped Graphene Nanosheets with Ultrahigh Pore Volume for High-Performance Supercapacitor. *Adv. Mater., Vol. 24*(41), P. 5610–5616.

98 Amiri, A. et al. (2015). Microwave-Assisted Synthesis of Highly-Crumpled, Few-Layered Graphene and Nitrogen-Doped Graphene for Use as High-Performance Electrodes in Capacitive Deionization. *Sci Rep., Vol. 5*(1), P. 17503.

99 Chang, L., Fei, Y. & Hu, Y.H. (2021). Structurally and chemically engineered graphene for capacitive deionization. *J. Mater. Chem. A., Vol. 9*(3), P. 1429–1455.

100 Zhang, M. & Kong, W. (2020). Recent progress in graphene-based and ion-intercalation electrode materials for capacitive *deionization*. *Journal of Electroanalytical Chemistry, Vol. 878,* P. 114703.

101 Liu, Y. et al. (2023). Electrosorption performance on graphene-based materials: a review. *RSC Adv., Vol. 13*(10), P. 6518–6529.

102 Younes, H. et al. (2022). Review on 2D MXene and graphene electrodes in capacitive deionization. *Environmental Technology & Innovation, Vol. 28,* P. 102858.

103 Byles, B.W. et al. (2018). Tunnel structured manganese oxide nanowires as redox active electrodes for hybrid capacitive deionization. *Nano Energy, Vol. 44,* P. 476–488.

104 Peng, W. et al. (2020). Fabrication of 3D flower-like MoS2/graphene composite as high-performance electrode for capacitive deionization. *Desalination, Vol. 473,* P. 114191.

105 Srimuk, P. et al. (2017). Titanium Disulfide: A Promising Low-Dimensional Electrode Material for Sodium Ion Intercalation for Seawater Desalination. Chem. Mater. American Chemical Society, Vol. *29*(23), P. 9964–9973.

106 Srimuk, P. et al. (2018). Potential-Dependent, Switchable Ion Selectivity in Aqueous Media Using Titanium Disulfide. *ChemSusChem., Vol. 11*(13), P. 2091–2100.

107 Lee, J. et al. (2017). Pseudocapacitive Desalination of Brackish Water and Seawater with Vanadium-Pentoxide-Decorated Multiwalled Carbon Nanotubes. *ChemSusChem, Vol. 10*(18), P. 3611–3623.

108 Srimuk, P. et al. (2018). Two-Dimensional Molybdenum Carbide (MXene) with Divacancy Ordering for Brackish and Seawater Desalination via Cation and Anion Intercalation. ACS Sustainable Chem. Eng. American Chemical Society, Vol. *6*(3), P. 3739–3747.

109 Rajagopalan, R. et al. (2020). Advancements and challenges in potassium ion batteries: A comprehensive review. *Adv. Funct. Mater., Vol. 30*(12), P. 1909486.

110 Yue, Z., Gao, T. & Li, H. (2019). Robust synthesis of carbon@Na4Ti9O20 core-shell nanotubes for hybrid capacitive deionization with enhanced performance. Desalination, *Vol. 449*, P. 69–77.

111 Cao, J. et al. (2019). Na3V2(PO4)3@C as Faradaic Electrodes in Capacitive Deionization for High-Performance Desalination. *Nano Lett. American Chemical Society, Vol. 19*(2), P. 823–828.

112 Jiang, Y. et al. (2020). A Review of Battery Materials as CDI Electrodes for Desalination. *Water, Vol. 12*(11), P. 3030.

113 Ntakirutimana, S. et al. (2020). Activated Carbon Electrode Design: Engineering Tradeoff with Respect to Capacitive Deionization Performance. *J. Electrochem. Soc., Vol. 167*(14), P. 143501.

114 Nam, D.-H. & Choi, K.-S. (2017). Bismuth as a New Chloride-Storage Electrode Enabling the Construction of a Practical High Capacity Desalination Battery. *J. Am. Chem. Soc. American Chemical Society, Vol. 139*(32), P. 11055–11063.

115 Pasta, M. et al. (2012). A Desalination Battery. Nano Lett. *American Chemical Society, Vol. 12*(2), P. 839–843.

116 Cohen, I. et al. (2013). Long term stability of capacitive de-ionization processes for water desalination: The challenge of positive electrodes corrosion. *Electrochimica Acta, Vol. 106,* P. 91–100.

117 Lu, D., Cai, W. & Wang, Y. (2017). Optimization of the voltage window for long-term capacitive deionization stability. *Desalination. Vol. 424,* P. 53–61.

118 Bayram, E. & Ayranci, E. (2011). A systematic study on the changes in properties of an activated carbon cloth upon polarization. *Electrochimica Acta, Vol. 56*(5), P. 2184–2189.

119 Srimuk, P. et al. (2017). Enhanced performance stability of carbon/titania hybrid electrodes during capacitive deionization of oxygen saturated saline water. *Electrochimica Acta, Vol. 224,* P. 314–328.

120 Xu, X. et al. (2020). Unprecedented capacitive deionization performance of interconnected iron–nitrogen-doped carbon tubes in oxygenated saline water. *Mater. Horiz, Vol. 7*(5), P. 1404–1412.

121 Tang, W. et al. (2017). Comparison of Faradaic reactions in capacitive deionization (CDI) and membrane capacitive deionization (MCDI) water treatment processes. *Water Research, Vol. 120,* P. 229–237.

122 임지원 et al. (2017). Flow channel design of capacitive deionization unit: pat. KR101721697B1 USA.

123 문형민 et al. (2021). Electro deionization-type water treatment apparatus: pat. KR102220165B1 USA.

124 Juzkow, M. et al. (2020). Liquid treatment using capacitive systems: pat. US10538437B1 USA.

125 Wal, A. van der et al. (2021). Apparatus and method for removal of ions: pat. US11168009B2 USA.

126 Sun, Z. et al. (2016). Membrane enhanced deionization capacitor device: pat. US9272926B2 USA.

127 오현제, 안주석, 정우식. (2021). Capacitive deionization electrode module of roll type, and water treatment apparatus: pat. KR102300797B1 USA.

128 황태문 et al. (2021). Energy self-sufficient system for treating high density salty waste water and side stream using membrane capacitive deionization (mcdi) module: pat. KR102274447B1 USA.

129 Linnartz, C.J., Rommerskirchen, A. & Wessling, M. (2022). Electrochemical module comprising a flexible membrane-electrode assembly: pat. EP3877341B1 USA.

130 Kim, D. et al. (2018). Continuous flow-electrode system, and high-capacity power storage and water treatment method using the same: pat. US9963363B2 USA.

131 Wessling, M., Gendel, Y. & Rommerskirchen, A. (2016). Single module, flow-electrode apparatus and method for continous water desalination and ion separation by capacitive deionization: pat. WO2016113139A1 USA.

132 노현철, 권태옥, 진채현. (2021). Composite electrochemical brackish water desalination system combining electrodialysis and capacitive deionization process: pat. KR102250944B1 USA.

133 柳丽芬, 苑丽新. (2021). Method for removing heavy metals and organic matters through capacitive deionization coupling electrocatalysis cooperation: pat. CN108423776B USA.

134 홍승관, 곽기문, 김인혁. (2020). Membrane Capacitive Deionization-Forward Osmosis Hybrid System for Precious Metal Recover: pat. KR102129493B1 USA.

135 김영오, 최정훈, 이한샘. (2019). Treating apparatus and method for concentrated waste water using ro-cdi process: pat. KR101981019B1 USA.

136 Bordain, Y.C. et al. (2019). Photovoltaic desalination system: pat. US10361329B2 USA.

137 김홍일 et al. (2019). Desalination module apparatus using a fabric electrode: pat. KR102003373B1 USA.

138 Wal, A.V.D. & Dlugolecki, P.E. (2013). A reverse capacitative de-ionisation apparatus and method for generating electricity: pat. EP2607321A1 USA.

139 Wal, A. van der et al. (2014). Apparatus for removal of ions comprising multiple stacks: pat. US20140048418A1 USA.

140 Sullivan, J.P. (2010). Method of Operating A Capacitive Deionization Cell Using Gentle Charge: pat. US20100065438A1 USA.

141 Hasseler, T.D. et al. (2020). Process design tools and techno-economic analysis for capacitive deionization. Water Research. *Vol. 183,* P. 116034.

142 Vineyard, D. et al. (2021). Life cycle assessment of electrodialysis for sidestream nitrogen recovery in municipal wastewater treatment. Cleaner Environmental Systems, *Vol. 2,* P. 100026.

А. Захаров[1], А. Тукешева[1,2], Сайед Фахад Бин Хак[3], Джон Феррарис[3], А. Захидов[3],
Т. Тажибаева[2], Т. Базарбаева[2], В. Павленко[1,2*]

Сулы ерітінділерді сыйымдылықты ионсыздандыру технологиясының қазіргі жағдайына шолу

Таза судың қолжетімділігі XXI ғасырдағы басты технологиялық, әлеуметтік және экономикалық міндеттердің бірі. Дүние жүзінде жер асты суларын өндірудің артуы тұзды судың бұлақтар мен сулы горизонттарға біртіндеп енуіне әкеледі. Бұл суды өнеркәсіп пен ауыл шаруашылығында техникалық су ретінде немесе ауыз су ретінде пайдалану үшін алдымен оны тазартып, минералсыздандыру қажет. Осылайша, тұздылығы әртүрлі суларды, әлсіз тұздыдан теңізге дейін тұзсыздандыру әдістері бірінші орынға шығады. Жүргізіліп жатқан зерттеулердің жалпы мақсаты тұзсыздандыру технологияларын, яғни энергияны тиімдірек және үнемді ету. Осы талаптарға жауап беретін перспективті технологиялардың бірі — суды сыйымдылықпен деионизациялау. Бұл технология 30 жылдан астам уақыт бойы кеңінен танымал, бірақ соңғы жылдары ғана суды сыйымдылықпен деионизациялау бойынша зерттеулерде айтарлықтай прогреске қол жеткізілді. Бұл шолуда суды сыйымдылықпен деионизациялау үшін қазіргі уақытта әзірленген жасуша архитектурасын, көміртекті материалдардағы жетістіктер қарастырылған және осы технологияны коммерцияландырудың перспективалары мен қиындықтары талқыланған.

Кілт сөздер: ССД, сыйымдылық деионизациясы, көміртекті материалдар, кеуекті көміртектер, көміртекті электродтар, фарадей электродтары.

А. Захаров, А. Тукешева, Сайед Фахад Бин Хак, Джон Феррарис, А. Захидов,
Т. Тажибаева, Т. Базарбаева, В. Павленко

Обзор современного состояния технологии емкостной деионизации водных растворов

Доступность чистой воды является одной из ключевых технологических, социальных и экономических проблем XXI века. Увеличение добычи подземных вод во всем мире приводит к постепенному проникновению соленой воды в источники и водные горизонты. Для использования этой воды в качестве технической в промышленности и сельском хозяйстве или в качестве питьевой воды она должна быть предварительно очищена и обессолена. Таким образом, на передний план выходят методы опреснения вод разной солености: от слабосоленых до морских. Общая цель текущих исследований состоит в том, чтобы сделать технологии опреснения воды более энергоэффективными и рентабельными. Одной из перспективных технологий, отвечающей этим требованиям, является емкостная деионизация воды (ЕДВ). Эта технология широко известна уже более 30 лет, однако только в последние годы был достигнут значительный прогресс в исследованиях ЕДВ. В этом обзоре мы рассмотрели разработанные в настоящее время архитектуры ячеек ЕДВ, достижения в области углеродных материалов, а также перспективы и проблемы коммерциализации этой технологии.

Ключевые слова: ЕДВ, емкостная деионизация, углеродные материалы, пористые угли, угольные электроды, фарадеевские электроды.